Digitized by the Internet Archive
in 2009 with funding from
University of Toronto

http://www.archive.org/details/s5philosophicalm32lond

57

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

CONDUCTED BY

SIR WILLIAM THOMSON, KNT. LL.D. P.R.S. &c.

GEORGE FRANCIS FITZGERALD, M.A., Sc.D., F.R.S.

AND

WILLIAM FRANCIS, PH.D. F.L.S. F.R.A.S. F.C.S.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

VOL. XXXII.—FIFTH SERIES.

JULY—DECEMBER 1891.

LONDON:

TAYLOR AND FRANCIS, RED LION COURT, FLEET STREET.

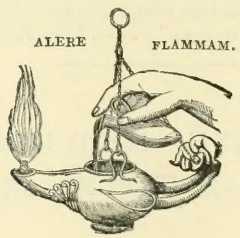
SOLD BY SIMPKIN, MARSHALL, HAMILTON, KENT, AND CO., LD.; AND WHITTAKER AND CO.;—AND BY ADAM AND CHARLES BLACK, AND T. AND T. CLARK, EDINBURGH; SMITH AND SON, GLASGOW;—HODGES, FIGGIS, AND CO., DUBLIN;—PUTNAM, NEW YORK;—VEUVE J. BOYVEAU, PARIS;—AND ASHER AND CO., BERLIN.

"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazmium.

22824



Q
1
P4
ser. 5
v. 32

CONTENTS OF VOL. XXXII.

(FIFTH SERIES).

NUMBER CXCIV.—JULY 1891.

	Page
Mr. J. Swinburne on some Points in Electrolysis	1
Mr. A. Schuster's Electrical Notes	9
Mr. S. U. Pickering on the Theory of Dissociation into Ions, and its Consequences	20
Dr. G. Gore on Changes of Voltaic Energy of Alloys during Fusion	27
Mr. W. Sutherland on a Kinetic Theory of Solids, with an Experimental Introduction	31
Mr. W. C. D. Whetham on Kohlrausch's Theory of Ionic Velocity	43
Mr. J. McCowan on the Solitary Wave	45
Mr. S. T. Preston on an Acoustic Thermometer—a Suggestion	58
Mr. R. A. Lehfeldt on a Modified Form of Wheatstone's Bridge	60
Prof. J. Perry on a Steam-Engine Indicator for High Speeds	63
Mr. R. T. Glazebrook on the Value of some Mercury Resistance Standards	70
Mr. J. E. Trevor on the Mutual Solubility of Salts in Water	75
Mr. S. Skinner on an Apparatus for Measuring the Compressibility of Liquids	79
Mr. F. T. Trouton on the Influence the Size of the Reflector exerts in "Hertz's Experiment"	80
Mr. S. U. Pickering on Mr. Sydney Lupton's Method of Reducing the Results of Experiments	90
Mr. E. H. Hayes's Consideration of some of the Objections raised by Mr. Lupton to Mr. Pickering's Methods of reducing Experimental Results	99
Mr. H. L. Callendar on the Construction of Platinum Thermometers	104
Dr. E. Obach on a probable Relationship between Specific Inductive Capacity and Latent Heat of Vaporization	113
Mr. F. J. Smith on an Instrument for Measuring Chronograph Traces	126

Page

Notices respecting New Books:—
Mr. Denning's Telescopic Work for Starlight Evenings . 127
Dr. Routh's Treatise on Analytical Statics 129
Mr. Dixon's Foundations of Geometry 130
M. Hermite's Explication de l'époch Quaternaire sans Hypothèses 131
Proceedings of the Geological Society:—
Messrs. A. V. Jennings and G. J. Williams on Manod and the Moelwyns 133
Mr. G. W. Lamplugh on the Drifts of Flamborough Head 133
Mr. A. Strahan on a Phosphatic Chalk with *Belemnitella quadrata* at Taplow 134
Prof. H. A. Nicholson and Mr. J. E. Marr on the Cross Fell Inlier 135
Mr. B. Hobson on the Igneous Rocks of the South of the Isle of Man 135
Prof. T. G. Bonney and Major-General C. A. McMahon on the Results of an Examination of the Crystalline Rocks of the Lizard District 136
Mr. F. Rutley on a Spherulitic and Perlitic Obsidian from Pilas, Jalisco, Mexico 137
Mr. E. Wilson on a Rhætic Section at Pylle Hill or Totter Down, Bristol 138
Mr. E. Wethered on a Microscopic Study of the Inferior Oolite of the Cotteswold Hills, including the Residues insoluble in Hydrochloric Acid 138
Dr. H. Hicks on some recently exposed Sections in the Glacial Deposits at Hendon 139
Rev. A. Irving on some Recent Excavations in the Wellington College district 140
Mr. A. Bell on some Post-Tertiary Marine Deposits on the South Coast of England 140
On the Analysis of the Light diffused by the Sky, by A. Crova. 141

NUMBER CXCV.—AUGUST.

Prof. W. Ostwald on Chemical Action at a Distance 145
Dr. G. Gore on the Relation of Volta Electromotive Force to Latent Heat, Specific Gravity, &c. of Electrolytes 157
Prof. J. Perry on the Study of Transformers 168
Prof. J. Perry on Mr. Blakesley's Method of Measuring Power in Transformers 185
Mr. J. Parker on the Theory of Magnetism and the Absurdity of Diamagnetic Polarity 192

Page

Prof. W. E. Ayrton and Dr. W. E. Sumpner on Alternate Current and Potential Difference Analogies in the Methods of Measuring Power 204
Mr. W. Sutherland on a Kinetic Theory of Solids, with an Experimental Introduction 215
Notices respecting New Books :—
Mr. G. F. Becker on the Structure of a Portion of the Sierra Nevada of California 226
Mr. G. F. Becker on Antiquities from under Tuolumne Table Mountain in California 226
Mr. G. F. Becker's Notes on the Early Cretaceous of California and Oregon 227
Mr. J. G. Hagen's The Photochronograph and its Application to Star-Transits 228
Proceedings of the Geological Society :—
Rev. E. Hill on Wells in West-Suffolk Boulder-clay 228
Mr. F. Rutley on the Melaphyres of Caradoc, with Notes on the Associated Felsites 229
Mr. J. J. Lister on the Geology of the Tonga Islands .. 229
Mr. C. Davison on the Inverness Earthquakes of November 15th to December 14th, 1890 230
On the Determination of the Dielectric Constant of Glass by aid of very rapid Electrical Oscillations, by R. Blondlot .. 230
On an Improved Method of determining Specific Heat by means of the Electrical Current, by Prof. Pfaundler 232

NUMBER CXCVI.—SEPTEMBER.

Mr. C. Chree on some Applications of Physics and Mathematics to Geology.—Part I. 233
Mr. J. Parker on the Theory of Magnetism and the Absurdity of Diamagnetic Polarity 253
Dr. A. Richardson on the Expansion of Chlorine by Light as applied to the Measurement of the Intensity of Rays of High Refrangibility. (Plates III. & IV.) 277
Mr. A. P. Chattock on the Electrification of Steel Needle-Points in Air. (Plate V.) 285
Dr. A. W. Rücker on the Relation between the Density and Composition of Dilute Sulphuric Acid 304
Sir G. G. Stokes on the Theory of the Solitary Wave 314
Notices respecting New Books :—
Profs. Oliver, Wait, and Jones's Treatises on Trigonometry and on Algebra 316
Prof. Jones's Logarithmic Tables 316
Dr. H. B. Fine's The Number-System of Algebra treated Theoretically and Historically 317
Mr. E. W. Hobson's Treatise on Plane Trigonometry .. 317

Page
Editorial Note on Mr. Parker's Paper on the Absurdity of Diamagnetism 318
On Homologous Spectra, by J. S. Ames 319
Magneto-Optic Phenomenon, by R. Sissingh 320

NUMBER CXCVII.—OCTOBER.

Prof. J. J. Thomson on the Discharge of Electricity through Exhausted Tubes without Electrodes 321
Mr. M. Carey Lea on Allotropic Silver 337
Mr. C. Chree on some Applications of Physics and Mathematics to Geology.—Part II. 342
Messrs. W. C. Roberts-Austen and A. W. Rücker on the Specific Heat of Basalt 353
Dr. J. Walker on the New Theories of Solution 355
Mr. H. M. Vernon on a New Modification of Phosphorus .. 365
Messrs. J. Walker and J. L. S. Hatton on an Experimental Determination of the Beats in the Vibrations of a Revolving Bell 370
Sir W. Thomson on Periodic Motion of a Finite Conservative System 375
Mr. F. J. Smith on some of the Effects of Magnetism on Rods of Iron, Nickel, and other Metals which have received a permanent Torsional Set; and a new form of Chronograph Stylus 383
Notices respecting New Books:—
Dr. H. Whiting's Course of Experiments in Physical Measurement.—Part III. Principles and Methods .. 396
Mr. T. W. Backhouse's Structure of the Sidereal Universe 397
Retinal Oscillations, by M. Charpentier 397
Lecture-illustration of Complementary Colours, by Nik. von Klobukow 399
On a Remarkable New Acid, by Th. Curtius 400

NUMBER CXCVIII.—NOVEMBER.

Messrs. E. L. Nichols and B. W. Snow on the Influence of Temperature on the Colour of Pigments 401
Lord Rayleigh on Dynamical Problems in Illustration of the Theory of Gases 424
Prof. J. J. Thomson on the Discharge of Electricity through Exhausted Tubes without Electrodes 445

Page
Mr. C. Tomlinson's Remarks suggested by a popular Article on the Ignis Fatuus 464
Sir W. Thomson on a Theorem in Plane Kinetic Trigonometry suggested by Gauss's Theorem of Curvatura Integra 471
Messrs. J. A. Wanklyn, W. Johnstone, and W. J. Cooper on the Nature of Solution 473
Notices respecting New Books:—
Dr. P. Molenbroek's Theorie der Quaternionen 477
Chemical Action at a Distance, by S. U. Pickering 478
Measurement of the Chemical Intensity of the Solar Radiation, by A. Bartoli 480
On Wheatstone's Determination of the Velocity of Electricity, by Prof. J. Stefan 480

NUMBER CXCIX.—DECEMBER.

Prof. C. A. Carus Wilson on the Influence of Surface-Loading on the Flexure of Beams. (Plate II.) 481
Mr. J. Trowbridge on the Damping of Electrical Oscillations on Iron Wires 504
Table of Zonal Spherical Harmonics, calculated by Messrs. C. E. Holland, P. R. Jones, and C. G. Lamb. With a short Explanation and some Illustrations of its use by Prof. J. Perry (Plate I.) 512
Mr. W. Sutherland on a Kinetic Theory of Solids, with an Experimental Introduction 524
Mr. J. McCowan's Note supplementary to a Paper on the Solitary Wave 553
Sir W. Thomson on Instability of Periodic Motion, being a continuation of Article on Periodic Motion of a finite Conservative System 555
Notices respecting New Books:—
Dr. H. Whiting's Course of Experiments in Physical Measurement.—Part IV. Appendix for the Use of Teachers 561
Molecular Theory of Diffusion and Electrolysis, by E. Riecke. 562
Method of Determining the Surface-Tension of Mercury, by H. Sentis 564
Allotropic Silver, by M. C. Lea 564

Index 565

PLATES.

I. Illustrative of Prof. J. Perry's Paper on a Table of Zonal Spherical Harmonics.

II. Illustrative of Prof. C. A. Carus Wilson's Paper on the Influence of Surface-Loading on the Flexure of Beams.

III. & IV. Illustrative of Dr. A. Richardson's Paper on the Expansion of Chlorine by Light as applied to the Measurement of the Intensity of Rays of High Refrangibility.

V. Illustrative of Mr. A. P. Chattock's Paper on the Electrification of Steel Needle-Points in Air.

ERRATA.

Page 27, line 8 from bottom, *for* incredible *read* inscrutable.
„ 438, top line, insert t' between "when" and "is."

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

JULY 1891.

I. *Some Points in Electrolysis.* *By* J. SWINBURNE*.

LET a cell be considered, with its external circuit closed through a resistance so high that in comparison the internal resistance is negligible. The cell discharges, and in passing from one pole to the other each coulomb does a certain quantity of work proportional to the difference of potential of the poles, E. This is really a mere definition: if difference of electric potential between two points is defined as what is measured by the work done on unit quantity of electricity passing from one to the other, the work done is numerically equal to E. The work done on the coulomb passing onward through the cell to regain its original position is equal to the work done when it passes through the external resistance. This work done on the coulomb may be supplied at the expense of chemical energy, or there may be local cooling somewhere. There may be chemical energy supplied at some points, and absorbed at others, and heat may disappear at some points, and may be evolved at others, but the algebraical sum comes out equal to E. Call the poles of the cell p and n, the positive pole being, for example, platinum and the negative such a metal as zinc, and suppose the electrolyte to be one homogeneous fluid. Part of the work done on the coulomb in passing from n to the electrolyte may be supplied chemically and may be called E_{nc}, another part may be supplied by local cooling E_{nh}, c standing for chemical

* Communicated by the Physical Society: read March 20, 1891.

and h for heat. If there is really local heating this will be negative. There is no work done by the homogeneous electrolyte, and the work done on it, in overcoming its resistance, is assumed to be inappreciable. The work done on the coulomb passing from the electrolyte to the plate forming the pole p is similarly $E_{pc}+E_{ph}$. We have thus

$$E=E_{pc}+E_{nc}+E_{ph}+E_{nh}.$$

First assume that the chemical work done is not dependent on the temperature of the cell. Let it discharge one coulomb at temperature θ_1 and do work equal to E_{θ_1} joules; E_{θ_1} being the electromotive force of the cell at that temperature. Of this work $E_{nc\theta_1}+E_{pc\theta_1}$ is supplied by chemical changes, and $E_{nh\theta_1}+E_{ph\theta_1}$ by cooling of the cell. Let the cell now be heated to the temperature θ, and let it be treated as a secondary element, and charged with one coulomb. The work done upon the cell is then E_θ; so

$$E_\theta=E_{nc\theta}+E_{pc\theta}+E_{nh\theta}+E_{ph\theta}.$$

The chemical work $E_{nc\theta}$ and $E_{pc\theta}$ is common to both processes. If E_θ were equal to E_{θ_1}, the same work would be done at the two temperatures, or $E_{nh\theta_1}+E_{ph\theta_1}$ would be equal to $E_{nh\theta}+E_{ph\theta}$.

But on letting the temperature of the cell fall to θ_1 again $\frac{\theta-\theta_1}{\theta}(E_{nh\theta}+E_{ph\theta})$ is available for external work; so that we should have perpetual motion. E_θ must therefore be greater than E_{θ_1}, so that a margin is allowed for the available work. We thus, by simple reasoning, arrive at Helmholtz's equation,

$$E=E_{nc}+E_{pc}+\theta\frac{dE}{d\theta}.$$

The electromotive force needed to do the chemical work may also vary with the temperature. For instance, if the chemical changes involved in discharging are brought about in a calorimeter at different temperatures, different heats may be evolved. Suppose E_{nc} and E_{pc} are less at a high temperature, and suppose at the lower temperature θ_1 there are no Peltier effects at the plates, so that, for that temperature at least, the cell obeys Sir William Thomson's law. If the cell could be charged at θ with a low electromotive force of $E_{e\theta}$, needed to bring the chemical changes about, and then discharged at θ, with a higher electromotive force, perpetual motion would be obtained. There must therefore be an absorption of electric energy at θ in addition to that needed

to produce the chemical work. This must be liberated as heat, and some of this must be available; the cell must therefore not only have a Peltier effect at the higher temperature, but though the chemical work done at that temperature is less, the electromotive force must actually be greater. By taking a cell whose E_c varies with the temperature round the usual Carnot cycle, we get

$$\frac{dE}{d\theta} = \frac{E_h}{\theta} - \frac{dE_c}{\theta},$$

which shows that the temperature-coefficient of the cell is not affected by the variation of chemical work with the temperature. The term $-dE_c/\theta$ is the remains of the extra work that had to be allowed in compensating for the reduction of the chemical work in the example just taken. Cutting it out we get

$$E_h = \theta \frac{dE}{d\theta},$$

or

$$E = E_c + \theta \frac{dE}{d\theta},$$

which is Helmholtz's equation again. Writing the equation in full, with separate terms for the poles, we have

$$E_n + E_p = E_{nc} + E_{pc} + \theta \frac{dE_n}{d\theta} + \theta \frac{dE_p}{d\theta}.$$

The cell may be made up with the plates in separate vessels with a tube of electrolyte to connect them; and the vessels can be heated to different temperatures. As E_n, E_{nc}, and $\theta \frac{dE_n}{d\theta}$ depend on the temperature of their vessel, the last equation can be split up into two:—

$$E_n = E_{nc} + \theta \frac{dE_n}{d\theta} \text{ or } E_{nh} = \theta \frac{dE_n}{d\theta},$$

and

$$E_p = E_{pc} + \theta \frac{dE_p}{d\theta} \text{ or } E_{ph} = \theta \frac{dE_p}{d\theta};$$

and, as the temperature-coefficient of each contact can be found, the Peltier effect at each contact can be obtained separately.

The hypothetical cell discussed has only one fluid, and is reversible. It might be difficult to find such a cell. If two fluids are used, their junction can be arranged in a third

intermediate vessel, and their Peltier effect, or difference of potential due to heat-formation, may be found as in the case of the plates.

Several workers, for instance M. Bouty and H. Gockel, have been investigating and measuring the temperature-coefficient or the Peltier effect directly.

Prof. J. Willard Gibbs has, of course, discussed the subject. In a letter to Dr. Lodge* he took a theoretical case in which this cell could be heated to the temperature of dissociation. He has written a second letter going more fully into the subject†.

This leads at once among the various conflicting views of electrolysis. One view, which seems tenable, is that electrolysis is always a case of double decomposition : that there is really a change. According to orthodox chemistry, if 2HCl is electrolysed H_2 and Cl_2 are obtained, and not 2H and 2Cl. The hydrogen and chlorine form combinations with themselves. Dissociation does not always split a compound in the same way as electrolysis, and the results of it are often "free atoms." It might be urged that in such a case as the electrolysis of NH_4Cl free atoms of NH_4 cannot exist, so NH_3 and HCl are produced by a sort of secondary action.

The cells discussed have been assumed to be reversible ; and some question may arise as to what the chemical work means. For instance, in a Daniell cell are we to take such data as Zn,O = 85,430 and Cu,O = 37,160‡ from a convenient treatise on Thermochemistry, and to consider that the conversion into sulphate and other actions in the cell are secondary? It is to be regretted that writers on Thermochemistry seldom give their data so that their meaning is clear. Zn,O, for instance, often means that metallic zinc is burned in gaseous oxygen. Allowance must then be made for the physical states of the components before, and of the products after the combination.

Returning to the reversible cell, however, before discharging a coulomb there are certain quantities of certain substances in certain physical and chemical conditions. After the discharge certain chemical and physical changes have taken place. Suppose any one of these is a secondary, or non-adjuvant action. For instance, suppose in discharging a Daniell cell that the conversion of zinc into oxide is a primary action, and the conversion of zinc oxide into zinc sulphate secondary or

* B. A. Report, 1886, p. 388.

† B. A. Report, 1888, p. 343.

‡ J. Thomsen, *Thermochemische Untersuchungen*, iii. pp. 275 and 320.

non-adjuvant. Some heat will be evolved, and the change from oxide to sulphate will not appear as external electrical work. On charging again there is only enough electromotive force at that contact to cope with the attraction of zinc for oxygen and not with the greater attraction for SO_4. The result is that the cell is not reversible. Any secondary or non-adjuvant action in the cell thus means non-reversibility. We thus have to deal not merely with Zn,SO_4 or ZnO,SO_3aq, and so on, but in a reversible cell, like a Daniell, we have to consider the attraction of Zn for SO_4; the physical change of Zn from a solid to a liquid state, which is generally included in the "heat of combination," as given; the solution of the $ZnSO_4$; and perhaps such small matters as change of volume of the cell. The copper salts must be dealt with similarly. Even if the heat of solution were non-adjuvant the cell would not be reversible.

Since 1883 I believe I have been alone in holding that not only is lead sulphate formed on both plates of a secondary battery, as shown by Dr. Gladstone and Mr. Tribe in 1882, but that its formation is the cause of the action of the cell, and not a secondary reaction at all. That is to say, there is no intermediate formation of PbO. To find out E_c of a cell we must open a sort of book. On one side put the heat of formation of every compound formed on discharge, and on the other of every compound broken up on discharge; the balance, including the physical changes, giving E_c. For instance, in a storage cell we credit the formation of $PbSO_4$ on the spongy plate, including, of course, the change of the SO_4 into the solid state, and on the peroxide plate we again credit $PbSO_4$. Two equivalents of H_2O are also credited. Two equivalents of H_2SO_4+Aq are debited, also two equivalents of H_2SO_4, and one equivalent of PbO_2, allowing for the O_2 becoming liquid.

It has been repeatedly urged that as the formation of $PbSO_4$ takes place on both plates it must cancel out. As in the case of a Daniell cell we have to deal with the difference between the heat of formation of two sulphates, it is assumed we must also deal with differences in a secondary battery. A little consideration will show, however, that the cases are different. In a discharging Daniell sulphate of zinc is formed and sulphate of copper is decomposed, so one goes on the credit side, the other on the debit. In a secondary battery sulphate is formed on both plates on discharge, and is therefore credited twice.

The doctrine of the Conservation of Energy also teaches us that electrolytic or nascent oxygen and hydrogen, which many

chemists regard as such valuable reagents, do not exist. What is the evidence in favour of the existence of nascent hydrogen? If some such metal as magnesium, or sodium amalgam, is put in dilute acid, bubbles come off. Many other metals act similarly. If such a compound as persulphate of iron is put in, too, it is reduced to proto-sulphate. From frequently observing effervescence when reduction is effected, it is easy to assume the effervescence is the cause of the reduction. The theory is that the energy supplied first produces hydrogen. A powerful attraction has just been overcome, and has been satisfied neither by combination with more hydrogen nor otherwise. The hydrogen then seizes on the persalt of iron, and takes away some of the acid radical, forming free acid, which in its turn acts on the oxide of the metal. This action is secondary, and may be supposed to evolve heat. There is thus waste of heat, and the cell is irreversible. A better explanation would be, that the metal can dissolve if it either reduces the persalt or evolves hydrogen. The reduction of the persalt needs less energy, so that takes place. When there is no reducible salt available, hydrogen is evolved; and as it has to be expanded into the gaseous form, a good deal of work has to be done on it. Evolution of hydrogen and reduction of the salt are thus alternate, not consecutive results. Similarly in an engine—the steam either works the engine or comes out at the safety-valve; it does not begin to lift the safety-valve, and then change its mind and work the engine in a nascent state. It must be remembered that the term oxidize has come to denote many other things than adding oxygen. For instance, adding any electronegative radical is called oxidizing. If sulphur had been as common as oxygen, no doubt we should always talk of sulphurizing. The use of the term "oxidize" has also led to the tacit assumption that in electrolysis the water is electrolysed and the other results are secondary actions of electrolytic oxygen and hydrogen. If there were such a thing as nascent hydrogen, putting a depolarizer, such as nitric acid, round the carbon plate of a Bunsen cell would not increase its electromotive force; it would merely make it heat more on discharge.

So far the cells considered have been reversible. It does not follow that a cell is always reversible, but, if not, there is at least one non-adjuvant action. As a good example of non-reversibility, aluminium and its solutions may be taken. Aluminium does not dissolve in dilute nitric or sulphuric acid, yet it cannot be deposited electrically from any known solution. Aluminium and carbon in nitric acid give only a small fraction of a volt.

From the definition of electromotive force adopted in this paper, the "seat of the electromotive force" is in the cell and not between the positive and negative metals outside. Yet the electrometer behaves as if there were a contact electromotive force. Dr. Lodge has attempted to explain this in accordance with the "chemical theory." He argues that when, for instance, zinc is exposed to the air, the oxygen either begins to combine with it, or actually combines with it, the particles of oxygen giving up their charge to the zinc on combining. This produces a difference of potential which increases till the oxygen's attraction for the zinc is counterbalanced by it. There is thus an electromotive force set up. Air being an insulator, the circuit is not completed. If the tendency to combine with oxygen can produce an electric stress which prevents combination, actual combination must either charge the metal, if insulated, or produce a current, if a path is allowed. If a clean piece of sodium is put on an insulating stand it goes on oxidizing, the amount of oxide formed corresponding to an enormous number of coulombs. Where do they go to? If the metal charges electrostatically, it must soon be millions and millions of volts below the potential of the air, and must discharge disruptively. Moreover, the millions of volts are far more than equivalent to Na_2O. Dr. Lodge assumes that a single element is an electrolyte, whereas a cell can only discharge by double decomposition. That is to say, to produce such an effect the metal must tear the oxygen from a combination, the other radical combining with another less electropositive metal, or removing an electronegative radical from it. It might be argued that zinc and copper plates in chlorine water will give a current, and chlorine is a single radical like oxygen. But immediately the plates are inserted the chlorine combines directly with both metals, without giving any current. A three-fluid battery is thus produced. The zinc is in a solution of zinc chloride, and the copper in copper chloride, and the intermediate liquid is chlorine water. The cell then discharges like a Daniell.

Though the oxygen form of the corrosion theory of contact electromotive force may not hold, it is quite possible that the Volta effect may be produced by thin films of water. Water is even more difficult to get rid of than oxygen, and might easily cause the electrometer readings. It must be remembered in connexion with this, that water must be present to enable even a combination of a metal with chlorine to take place. It is well known that dry chlorine will not attack a dry metal. Even sodium may be left in contact with chlorine.

Even if the Volta effect is due to the presence of traces of an electrolyte, such as water, and not to a non-electrolytic combination with free oxygen, the "seat of the electromotive force" still depends on a mere definition. The term "electromotive force" is continually used in two senses. It is sometimes used to denote the difference between the potentials of two points, and sometimes to denote the rate of fall of potential. Maxwell gives it the latter definition formally, but frequently writes of the electromotive force when he means the line-integral of the electromotive force, that is to say the difference of potential. In connexion with cells, "electromotive force" is always used to mean difference of potential, so the stricter meaning, rate of fall of potential, may be disregarded just now. If we define the difference of potential between two points as proportional to the work done on a unit quantity of electricity moving from one point to the other, we have a clear statement of what we mean. But if we attempt to make the measurement, we find the unit quantity of electricity must have some carrier; and when we use an electrometer, we do not measure the work done on a unit quantity of electricity moving from one point to the other; we really measure the work done when a particular conductor is used as carrier. It is not necessary to consider any part of the circuit as the seat of the electromotive force. There is a circuit, and the potential is cyclic. Similar cases occur in other branches of electricity. For instance, a "unipolar" dynamo may be made up of a rotating magnet with a stationary circuit. If the resistance of the internal circuit is negligible in comparison with that of the external, the whole expenditure of power is in the external circuit, and the fall of potential over the external resistance is sensibly the whole potential or electromotive force of the machine. There is, however, no way of finding the seat of this electromotive force. If the rotating magnet is supposed to carry "lines of induction" round with it, they cut the external circuit and produce electromotive force there, so that becomes the seat of the electromotive force. If the lines of induction are taken as stationary, the rotating part of the circuit cuts them and becomes the seat of the electromotive force. The effects on the external resistance are the same in both cases. If it is a voltmeter the readings are the same, and they remain so if the lines of induction rotate faster or slower than the magnet, or in the opposite direction. If the voltmeter is replaced by an electrometer, it is still impossible to say where the seat of the electromotive force is. The readings would be the same whether the lines of induction were stationary, or revolved and cut the leads to the elec-

trometer, or revolved and passed through the electrometer as if it were a zigzag gateway, without cutting the metallic part of the circuit anywhere. If the electrometer is removed and a proof-plate is used, by touching one terminal with it and measuring the work done when it moves to the other, the result is the same. If the lines are stationary, the proof-plate is charged by one terminal and repelled by it and attracted by the other. If the lines rotate, the proof-plate is urged forward by the lines of induction cutting it at right angles to its path. The reading is the same in both cases. The lines of induction are a mere convention, and there is no way of finding the seat of the electromotive force. All that can be said is that it is cyclic, and that the difference of potential of any two parts of the circuit of the same metal can be measured. In some cases the seat where power is spent can be determined, and in others it cannot.

Similarly in the cell, the seat of expenditure of power can sometimes be told, as when there is a resistance in circuit; sometimes it cannot, as when the cell works a unipolar, or, by extension, any other motor. The difference of potential between any two points of the same material can be measured, but all that can be said is that the electromotive force of the whole circuit is cyclic.

II. *Electrical Notes.*

By Arthur Schuster, *F.R.S.**

1. *The Vector Potential.*

THERE is a general tendency at present among electricians to dispense as much as possible with the "Vector Potential," but I believe that many of the difficulties which have led to the restriction of its use may be removed. At any rate there seems room for the following renewed discussion of some well-known equations.

I was led to the investigation through an attempt to find the magnetic effects of currents distributed through space in such a way that the lines of flow should be identical in form to the lines of induction in certain simple magnetic systems. We might, for instance, wish to find the components of magnetic force which are produced by currents in an unlimited homogeneous conductor, the electrical potential at every point being the same as the magnetic potential due to a simple magnetic shell. The case could be realized by a conductor in

* Communicated by the Author.

which a constant electromotive force is distributed over a finite surface.

Any one attempting the solution of such a problem would probably be led into the same difficulties which I encountered, and although he would doubtless soon get over them, the following discussion may save him some trouble.

I begin by writing down the well-known equations referring to the Vector Potential in Maxwell's form, taking in the first place the magnetic permeability as constant.

F, G, H being the components of the vector potential, u, v, w those of the current, we have

$$4\pi u = \frac{d}{dy}\left(\frac{dG}{dx} - \frac{dF}{dy}\right) - \frac{d}{dz}\left(\frac{dF}{dz} - \frac{dH}{dx}\right); \quad . \quad . \quad (1)$$

or, writing

$$J = \frac{dF}{dx} + \frac{dG}{dy} + \frac{dH}{dz},$$

$$4\pi u = \frac{dJ}{dx} - \nabla^2 F, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

with similar equations for v and w.

Putting

$$\left.\begin{aligned} F' &= \iiint \frac{u}{r}\, dx\, dy\, dz, \\ G' &= \iiint \frac{v}{r}\, dx\, dy\, dz, \\ H' &= \iiint \frac{w}{r}\, dx\, dy\, dz; \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\chi = \frac{1}{4\pi}\iiint \frac{J}{r}\, dx\, dy\, dz, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Maxwell concludes that

$$\left.\begin{aligned} F &= F' - \frac{d\chi}{dx}, \\ G &= G' - \frac{d\chi}{dy}, \\ H &= H' - \frac{d\chi}{dz}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This conclusion is not, however, justified. The second terms on the right-hand side of equations (5) disappear altogether from equations (1). If therefore F, G, H are solutions of (1), the value of χ is not restricted to that given

in (4), but is arbitrary. If, on the other hand, F′,G′, H′ are *not* solutions of (1), they cannot be converted into solutions by the terms involving χ.

That F, G, H, as given in (5), do not necessarily satisfy (1) may be shown as follows. Writing F_1, G_1, H_1 instead of F, G, H on the left-hand side of (5), we obtain from these equations,

$$\nabla^2 F_1 = \nabla^2 F' - \frac{d\nabla^2\chi}{dx};$$

and with the help of (3) and (4),

$$4\pi u = \frac{dJ}{dx} - \nabla^2 F_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Comparing this with

$$4\pi u = \frac{dJ}{dx} - \nabla^2 F, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

it is not correct to draw the conclusion that F_1 is a solution of (2), for equation (6) still involves on the right-hand side the quantities F, G, H. The correct conclusion is that

$$\nabla^2 F_1 = \nabla^2 F. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

We may treat equation (5) in a different way, and deduce from them

$$\frac{dF_1}{dx} + \frac{dG_1}{dy} + \frac{dH_1}{dz} = \frac{dF'}{dx} + \frac{dG'}{dy} + \frac{dH'}{dz} + J.$$

If, then, F_1, G_1, H_1 were equal to F, G, H, as Maxwell puts them, it would follow that

$$\frac{dF'}{dx} + \frac{dG'}{dy} + \frac{dH'}{dz} = 0; \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and this would show that F′, G′, H′ are solutions of (1) without the addition of the terms involving χ.

It may be shown that in all legitimate cases equation (8) is satisfied; but before proceeding to discuss the conditions on which this depends, I shall treat of a special case which will bring out clearly the points to which I wish to draw attention.

Let u, v, w be electric currents deducible from a current function ϕ such that

$$u = \frac{d\phi}{dx}, \quad v = \frac{d\phi}{dy}, \quad w = \frac{d\phi}{dz};$$

and let $\phi = \frac{x}{r^3}$.

The lines of flow in this case are identical in shape with the

lines of force due to an indefinitely small magnet of finite magnetic moment.

Substituting the above values of u, v, w into (3), it will be shown further on (13) that

$$\left.\begin{aligned} F' &= \frac{2\pi}{3r} - \frac{2\pi x^2}{r^3} \\ G' &= -\frac{2\pi xy}{r^3}, \\ H' &= -\frac{2\pi xz}{r^3}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

But these values of F′, G′, H′ neither satisfy equations (1), nor do they satisfy the condition $J=0$ for

$$\frac{dF'}{dx} + \frac{dG'}{dy} + \frac{dH'}{dz} = -\frac{8\pi}{3}\frac{x}{r^3}.$$

It seems well at this stage to investigate the conditions which have to be satisfied in order that $J=0$.

By a well-known transformation we obtain from equation (3),

$$\frac{dF'}{dx} + \frac{dG'}{dy} + \frac{dH'}{dz} = \iiint \frac{1}{r}\left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}\right) dx\,dy\,dz - \iint \frac{lu + mv + nw}{r}\, dS.$$

The triple integral vanishes, and the surface integral has to be taken over the boundary of the region which is considered. If this region includes all space which contains electric currents, the second integral will also vanish provided the space includes no singular points. In the example which has been given, however, $\phi = \frac{\sigma}{r^3}$, which makes the components infinitely large at the origin. If this point is excluded by an infinitely small sphere surrounding it, the surface integral in the above equation has to be taken over this infinitely small sphere and will be finite. It is owing to this fact that the condition

$$\frac{dF'}{dx} + \frac{dG'}{dy} + \frac{dH'}{dz} = 0$$

is not satisfied in the special case treated above.

This may perhaps be more clearly seen in another way. Maxwell's equations fall to the ground unless the currents flow everywhere in closed lines. The example we have chosen

violates that condition at the origin. For the current function $\phi = \frac{x}{r^3}$ represents the limiting case of a source and sink which are indefinitely approached to each other. If the source and sink are joined together by the linear current necessary to complete the circuit, the proper solution of the question may be obtained.

Take a system of currents due to a sink of electricity at A of strength 4π having a current function $\frac{1}{r_1}$, a source of strength 4π at B having a current function $-\frac{1}{r_2}$, and a linear current equal in intensity to 4π joining A and B. The value of F′ in that case would be

$$F' = \iiint \left(\frac{x_2}{r_2^3} - \frac{x_1}{r_1^3} \right) dx\, dy\, dz + \int \frac{4\pi}{r} ds,$$

when the last integral is to be taken over the line joining A and B. The integration gives

$$F' = -2\pi \left(\frac{x_1}{r_1} - \frac{x_2}{r_2} \right) + 4\pi \int \frac{ds}{r}.$$

If A and B approach each other indefinitely,

$$x_1 - x_2 = ds\ ;$$

and

$$F' = -2\pi \frac{d}{dx} \left(\frac{x}{r} \right) ds + \frac{4\pi ds}{r} = 2\pi ds \left(\frac{1}{r} + \frac{x^2}{r^3} \right)\ ;$$

the current function at the same time becomes

$$\phi = -\frac{x\, ds}{r^3}.$$

Corresponding to a current function $\phi = \frac{x}{r^3}$, we obtain therefore the values

$$\left.\begin{aligned} F &= -2\pi \left(\frac{1}{r} + \frac{x^2}{r^3} \right), \\ G &= -2\pi \frac{xy}{r^3}, \\ H &= -2\pi \frac{xz}{r^3}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (10)$$

These equations differ from those obtained before (9) by a quantity representing the effect of an indefinitely short

current at the origin, which current is necessary to complete the circuit as shown.

The values of F, G, H in (10) satisfy the condition

$$\frac{dF}{dx}+\frac{dG}{dy}+\frac{dH}{dz}=0,$$

and are therefore solutions of the problem. A comparison of (10) and (9) also shows that $\nabla^2F'=\nabla^2F$, agreeing with the conclusion previously arrived at (7).

In the expressions (9) the flow at the origin is taken to be parallel to the axis of X. The equations show that the Vector Potential may be expressed as the resultant of a vector $\frac{2\pi x}{r^2}$ directed towards the origin, and another $-\frac{2\pi}{r}$ along the axis of X. If, in the general case, λ, μ, ν are the direction-cosines of the axis of flow, the components of the Vector Potential are

$$\left.\begin{aligned} F&=-2\pi\left[\frac{\lambda}{r}+\frac{x}{r^3}(\lambda x+\mu y+\nu z)\right],\\ G&=-2\pi\left[\frac{\mu}{r}+\frac{y}{r^3}(\lambda x+\mu y+\nu z)\right],\\ H&=-2\pi\left[\frac{\nu}{r}+\frac{z}{r^3}(\lambda x+\mu y+\nu z)\right]. \end{aligned}\right\} \quad . \quad . \quad (11)$$

We are now prepared to deal with the problem indicated at the beginning of this paper. Imagine a magnet having an intensity of magnetization at a point ξ, η, ζ, measured by its components A, B, C. We wish to find the vector potential for a system of conductors flowing along the lines of induction of such a magnet; and having therefore a current potential identical with the magnetic potential due to A, B, C. The result is obtained directly from (11), by multiplying the right-hand side with $I d\xi\, d\eta\, d\zeta$, taking account of the change of origin and integrating throughout the space of the magnet. We find in this way

$$-\frac{1}{2\pi}F=\iiint\left\{\frac{A}{r}+\frac{(x-\xi)}{r^3}\left[A(x-\xi)+B(y-\eta)+C(z-\zeta)\right]\right\}d\xi\, d\eta\, d\zeta, \quad . \quad . \quad (12)$$

with corresponding expressions for G, and H.

For some purposes it may be more useful to expand the current potential in terms of solid harmonics, and we are

therefore led to find the vector potential for a system of currents,

$$u=\frac{d\phi}{dx},\quad v=\frac{d\phi}{dy},\quad w=\frac{d\phi}{dz},$$

when ϕ is a homogeneous function of degree n.

The following transformation will be useful :—

$$\nabla^2 r^2\frac{d\phi}{dx}=\frac{d\phi}{dx}\nabla^2 r^2+2\left(\frac{dr^2}{dx}\frac{d^2\phi}{dx^2}+\frac{dr^2}{dy}\frac{d^2\phi}{dx\,dy}+\frac{dr^2}{dz}\frac{d^2\phi}{dx\,dz}\right)+r^2\nabla^2\frac{d\phi}{dx}$$

$$=6\frac{d\phi}{dx}+4\left(x\frac{d^2\phi}{dx^2}+y\frac{d^2\phi}{dy\,dx}+z\frac{d^2\phi}{dz\,dx}\right)$$

$$=(4n+2)\frac{d\phi}{dx}.$$

Writing

$$\mathrm{F}'=\iiint\frac{u}{r}\,dx\,dy\,dz=\int\!\!\int\!\!\int\frac{d\phi}{dx}\cdot\frac{1}{r}\,dx\,dy\,dz,$$

we may satisfy the condition $\nabla^2\mathrm{F}'=-4\pi\dfrac{d\phi}{dx}$ by

$$\mathrm{F}'=-\frac{2\pi r^2}{2n+1}\frac{d\phi}{dx}\quad\ldots\ldots\quad(13)$$

with similar expressions for G′ and H′.

But these expressions do not satisfy the characteristic equation for the vector potential, and it is easily seen that the problem is indeterminate as long as we do not fix the manner in which the system of currents is completed at the origin. This will have to be determined in each case from the nature of the problem. From (13) we easily obtain

$$\frac{d\mathrm{F}'}{dx}+\frac{d\mathrm{G}'}{d\eta}+\frac{d\mathrm{H}'}{dz}=-\frac{4\pi}{2n+1}n\phi.$$

If F_1, G_1, H_1 are quantities satisfying the condition

$$\nabla^2\mathrm{F}_1=\nabla^2\mathrm{G}_1=\nabla^2\mathrm{H}_1=0,$$

and

$$\frac{d\mathrm{F}_1}{dx}+\frac{d\mathrm{G}_1}{dy}+\frac{d\mathrm{H}_1}{dz}=\frac{4\pi}{2n+1}\cdot n\phi.$$

The components $\mathrm{F}'+\mathrm{F}_1$, $\mathrm{G}'+\mathrm{G}_1$, $\mathrm{H}'+\mathrm{H}_1$, will satisfy all necessary conditions for the vector potential. The solution

may be effected in a number of different ways. For instance, we may make

$$F_1=\frac{4\pi n V}{2n+1},\quad G_1=0,\quad H_1=0,$$

when V is defined by $\phi=\dfrac{dV}{dx}$.

In this case the currents are completed at the origin by a flow parallel to the axis of X.

As regards the surface conditions to be satisfied by the vector potential, there seems no difficulty when the magnetic permeability is uniform throughout space, but for the surfaces of two media having a different permeability special considerations seem necessary. I am not aware that this point has been investigated.

If the medium through which the currents flow is subject to magnetic polarization, we may write for the vector potential at the point x, y, z,

$$F=\iiint\frac{u}{r}\,dx'\,dy'\,dz'+\iiint\left(B\frac{dp}{dz'}-C\frac{dp}{dy'}\right)dx'\,dy'\,dz', \quad (14)$$

where the components of the currents are functions of $x'\,y'\,z'$ and p is the reciprocal of the distance between x, y, z and x', y', z'.

A, B, C are the components of magnetization of the medium. If these are due to the distribution of currents alone, we have the additional equations

$$A=\kappa\alpha.\quad B=\kappa\beta,\quad C=\kappa\gamma.$$

α, β, γ being the components of magnetic force. Integrating the second term of (14) by parts and substituting

$$4\pi u=\frac{d\gamma}{dy}-\frac{d\beta}{dz},$$

the equation for the vector potential is obtained in the form

$$F=\iiint\frac{\mu u}{r}\,dx'\,dy'\,dz'+\iint\frac{1}{r}(Bn-Cm)dS, \quad . \quad (15)$$

when $\mu=1+4\pi\kappa$ and l, m, n are the direction-cosines of the normal drawn towards the outside of the element dS, the surface integral being taken over all surfaces at which two media of different magnetic properties join.

These equations differ from those given by Maxwell by the

second terms. These terms are of some importance, for Maxwell's expression cannot be made to satisfy the surface conditions, while the surface integrals in the equations (15) allow us to do so.

The expression $(Bn-Cm)$ may be considered as the component of a current which must be imagined to be distributed over the surfaces of separation of the two media.

In order to determine the discontinuities of the differential coefficients, let κ_1 and κ_2 be the magnetic susceptibility in the two media, and let l, m, n be the direction-cosines of the normal to the surface drawn towards the *inside* of the medium to which the index 1 refers. The surface currents are then given by

$$\left.\begin{aligned} u' &= m(\kappa_1\gamma_1-\kappa_2\gamma_2)-n(\kappa_1\beta_1-\kappa_2\beta_2),\\ v' &= n(\kappa_1\alpha_1-\kappa_2\alpha_2)-l(\kappa_1\gamma_1-\kappa_2\gamma_2),\\ w' &= l(\kappa_1\beta_1-\kappa_2\beta)-m(\kappa_1\alpha_1-\kappa_2\alpha_2). \end{aligned}\right\} \quad . \quad . \quad (16)$$

If the axis of z is taken in the direction of the normal, $w'=0$, and we conclude: The first differential coefficients of the *normal* component of the Vector Potential are continuous. The differential coefficients of F and G in the directions x and y must also be continuous, and the only ones which may be discontinuous are $\dfrac{dF}{dz}$ and $\dfrac{dG}{dz}$. The discontinuities may be written down from (15) and (16),

$$\frac{dF}{dz_1}+\frac{dF}{dz_2}=4\pi(\kappa_1\beta_1-\kappa_2\beta_2).$$

In this equation $\dfrac{dF}{dz_2}$ is written for the differential coefficients along the negative axis of z. But

$$\beta_1=\frac{1}{\mu_1}\left(\frac{dF}{dz_1}-\frac{dH}{dx}\right),$$

$$\beta_2=\frac{1}{\mu_2}\left(-\frac{dF}{dz_2}-\frac{dH}{dx}\right).$$

Hence

$$\frac{dF}{dz_1}+\frac{dF}{dz_2}=\frac{\mu_1-1}{\mu_1}\left(\frac{dF}{dz_1}-\frac{dH}{dx}\right)+\frac{\mu_2-1}{\mu_2}\left(\frac{dF}{dz_2}+\frac{dH}{dx}\right)$$

$$\frac{1}{\mu_1}\frac{dF}{dz_1}+\frac{1}{\mu_2}\frac{dF}{dz_2}=\left(\frac{1}{\mu_1}-\frac{1}{\mu_2}\right)\frac{dH}{dx} \quad . \quad . \quad . \quad . \quad (17)$$

Equation (17) is one of the required boundary conditions. The second is obtained by symmetry.

$$\frac{1}{\mu_1}\frac{dG}{dz_2}+\frac{1}{\mu_2}\frac{dG}{dz_2}=\left(\frac{1}{\mu_1}-\frac{1}{\mu_2}\right)\frac{dH}{dy}. \quad . \quad . \quad . \quad (18)$$

The two last equations complete the solution of the problem, as all other differential coefficients are continuous.

It is easy to show that the conditions we have found lead to the well-known continuity of the normal components of the induction and of the tangential components of the magnetic forces.

We have arrived at the conclusion that

$$F=\iiint\frac{\mu u}{r}\,dx\,dy\,dz+\iint\frac{u'}{r}\,dS, \quad . \quad . \quad . \quad (19)$$

with the corresponding equations for G and H will always give us correct expressions for the Vector Potential, u, v, w being the components of the given currents, and u', v', w' currents distributed over the boundaries between bodies of different magnetic permeabilities. F, G, H are not, however, the *only* solutions, but others may be obtained by addition of $\frac{d\chi}{dx}$, $\frac{d\chi}{dy}$, $\frac{d\chi}{dz}$, respectively, χ being arbitrary. It appears, however, that if u', v', w' in (19) are determined so as to satisfy the necessary boundary conditions, both χ and its first differential coefficients must be continuous throughout space. The function χ may therefore be expressed as a potential function of attracting matter distributed throughout space with an arbitrary volume-density, there being no surface distribution anywhere. If χ does not vanish it follows from (5) that

$$\frac{dF}{dx}+\frac{dG}{dy}+\frac{dH}{dz}=-\nabla^2\chi;$$

for it has been shown that whenever currents flow in closed circuits only,

$$\frac{dF'}{dx}+\frac{dG'}{dy}+\frac{dH'}{dz}=0.$$

If, then, the additional condition is imposed on the Vector Potential that

$$\frac{dF}{dx}+\frac{dG}{dy}+\frac{dH}{dz}$$

should vanish, its components become determinate in every respect.

Returning for a moment to the investigation which has led to equations (10), we may write the vector potential due to a conduction current 4π through a linear element ds at the origin, the currents being completed by displacement currents:—

$$F = 2\pi ds\left(\frac{1}{r} + \frac{x^2}{r^3}\right) = \left(\frac{4\pi}{r} - \frac{d}{dx}\frac{2\pi x}{r}\right)ds;$$

$$G = 2\pi ds\frac{xy}{r^3} \quad = \quad -\frac{d}{dy}\frac{2\pi x}{r}\,ds;$$

$$H = 2\pi ds\frac{xz}{r^3} \quad = \quad -\frac{d}{dz}\frac{2\pi x}{r}ds.$$

As far as the magnetic forces are concerned, the terms involving the differential coefficients disappear, and we might put equally well

$$F = \frac{4\pi ds}{r}, \quad G = 0, \quad H = 0.$$

If the conduction current is i instead of 4π, we obtain

$$F = \frac{ids}{r}, \qquad G = 0, \quad H = 0;$$

and this is exactly what we should have obtained if we had neglected the displacement currents altogether: a well-known result.

The following transformation seems of some interest. Consider electric currents in a system of bodies whether conductors or non-conductors, the magnetic permeability being uniform for the sake of simplicity. The Vector Potential at a point x, y, z will be

$$F = \int\int\int \frac{u}{r}\,da\,db\,dc$$

where the currents are given as functions of a, b, c.

Assume further the existence of a current function, from which the currents may everywhere be derived. Over certain surfaces the current function may be discontinuous. We put therefore

$$u = \frac{d\phi}{da}, \quad v = \frac{d\phi}{db}, \quad w = \frac{d\phi}{dc},$$

and form the equations for the components of magnetic

induction. It will be sufficient to carry out the transformation for one of the components :—

$$a = \frac{dH}{dy} - \frac{dG}{dz}$$

$$= \iiint \left(w \frac{d\frac{1}{r}}{dy} - v \frac{d\frac{1}{r}}{dz} \right) da\, db\, dc,$$

$$= \iiint v \frac{d\frac{1}{r}}{dc} - w \frac{d\frac{1}{r}}{db}\, da\, db\, dc;$$

and, finally, remembering that

$$\frac{dv}{dc} = \frac{dw}{db},$$

$$a = \iint \frac{mv - nv}{r}\, dS.$$

Similarly,

$$b = \iint \frac{nu - lw}{r}\, dS,$$

$$c = \iint \frac{lv - mu}{r}\, dS.$$

l, m, n are the normals drawn to the inside of each medium. The surface integration must be carried out on both sides of a surface at which u, v, w are discontinuous.

I do not know whether these equations will ever really simplify the investigation of an actual problem, but it seems of interest to know that we can always express the magnetic forces due to *steady* currents in a conductor, in terms of the values of the currents at the surface of the conductor ; the components of the currents inside may be unknown, though of course they are determined by the surface values.

III. *The Theory of Dissociation into Ions, and its Consequences.* *By* Spencer Umfreville Pickering, *M.A.*, *F.R.S.**

THE supporters of the present physical theory of solution hold that the majority of salts, acids, and bases, when dissolved in a large excess of water, are entirely resolved into their component ions. That the facts of the case warrant such

Communicated by the Physical Society : read March 20, 1891.

a conclusion I have already disputed (Phil. Mag. vol. xxix. p. 490, and 'Nature,' xlii. p. 626); but theoretical objections of a fundamental character can, I believe, be raised against this dissociation theory, and, though I have already alluded to these, they have not yet been fully discussed. Many of the questions which are asked in the following pages can no doubt be answered satisfactorily, but as far as I am aware this has not yet been done, and it is certainly incumbent on the supporters of the theory to give physicists and chemists a clear conception of what their theory involves.

When hydrochloric-acid gas, for instance, is dissolved in water, the molecules, which were intact to start with, become resolved into their ions, so that each of these acts as if it were a separate unit. This I believe is, according to the theory, the total and only change which occurs : the water remains in the same state in which it was to start with. The resolution of HCl into H and Cl atoms has been held of necessity to involve an *absorption* of heat, an absorption considerably in excess of that which we know occurs when it is resolved into hydrogen and chlorine molecules ; and, whether the ions are identical with free atoms or not, we have the positive statement of Arrhenius, the originator of the present dissociation theory, that the resolution of a body such as hydrochloric acid into its ions absorbs heat*. If then this, which is the only change, *absorbs* heat, whence comes the 17,300 cal. which are, as a matter of fact, *evolved* during dissolution ?

In the communication to which reference has been made, Arrhenius does not consider the thermal results of dissolution, and a subsequent consideration of these seems to have led some of the supporters of the theory to hold a view diametrically opposed to that just quoted. They now hold, I believe, that the decomposition of molecules into their ions *evolves* heat ; that that heat, which they still admit must be absorbed by the decomposition of the molecules into ordinary atoms, is more than counterbalanced by the combination of the atoms with electric charges. This change of front must rather be

* Arrhenius, *Bitrag till Kongl. Svenska Vetenskaps-Akademiens Handlingar*, Stockholm, 1883-4. Out of several sentences I may quote the following italicised passage :—" La transformation de l'état inactif en l'état actif d'un hydrate (faible) est accompagnée par une absorption de chaleur;" and the heat absorbed in the transformation is named " chaleur d'activité." The terms used in the above must be translated into the more modern language of the dissociationists, thus : inactive = undissociated; active = dissociated into ions; hydrate = any hydrogen compound, such as an acid or base ; feeble = not much dissociated. See also Lodge's epitome of Arrhenius's paper, B. A. Report, 1886, pp. 361-384.

inferred indirectly from the writings of dissociationists than from any definite retraction which they have published ; nor does it appear to have been followed by all the supporters of the theory, for the explanation given by Arrhenius of the constancy of the heat evolved on neutralizing acids with bases is that it is in all cases due to the combination of the ions H and OH to form H_2O, and this explanation was quoted as recently as September last (B. A. meeting) by Shaw as being one of the strongest arguments in favour of the theory. It may also be remarked that up to July 1889 Ostwald seems to have held both views, and to have adopted either just as the exigencies of the case suggested : he explains the normal heat of neutralization as being due to the heat evolved in the formation of a molecule from its ions ('Outlines of General Chemistry,' 1890, p. 368), and the abnormal heat of neutralization as being due to heat evolved in the formation of ions from a molecule, though not, of course, the same molecule as in the previous case (p. 369).

The first point, therefore, on which the dissociationists should give us definite information is, whether the dissociation of a molecule into ions is supposed to evolve or absorb heat.

Presupposing that the answer will be that heat is evolved (at any rate in cases similar to that of hydrochloric acid), their theory cannot be said to be *primâ facie* inconsistent with the conservation of energy ; but other very serious difficulties arise which call for explanation.

The idea of heat being evolved by the combination of a charge with an atom involves the conception that the charge is originally independent of the atom : indeed the main idea of the theory seems to lie in the distinction between an ion, or charged atom, and an ordinary or uncharged atom*. We may ask, therefore, whence come these charges? All the ordinary means by which bodies become charged seem to be absent in the present case. No external energy has been expended, no friction can be supposed to exist except such as might result indirectly from an attraction between the water and the acid ; but even if the existence of such an attraction were admitted, it could never cause sufficient friction to over-

* *Cf.* Ostwald, *loc. cit.*, p. 275 :—"What actually exists in the solution is single potassium atoms with enormous electrical charges. We do not know what those charges are in reality, but this we do know, that the chemical properties of substances are greatly altered by electrical charges. . . . As soon as the potassium atoms in solution lose their charge, as they do, for example, when led by an electric current to a platinum wire, where they can give up their electricity, potassium with its ordinary properties is at once produced, as is seen in its ability to decompose water with evolution of hydrogen."

come the very attraction which is the original cause of it, to say nothing of the still stronger attraction which holds the atoms together: induction cannot apply, as both water and acid are supposed to be uncharged to start with, and even if there were a contact difference of potential between these two substances, it would not result in communicating both the + and − charges to one only of the bodies brought into contact,—the acid.

In the second place, how can we imagine that an electric charge, which we must at present regard as an affection of matter, can combine with matter to produce heat and itself remain in *statu quo*? Such a view is little less than endowing the charges with some of the exclusive properties of matter, and calling this new matter into existence just when and where may be most convenient to the theory.

In the third place, how can it be maintained that the positive electrification of the hydrogen, and the negative electrification of the chlorine, would dissolve the union between them? According to all our experience of electricity, such electrification would make them cling together all the more firmly. Further, if these so-called + and − charges repel each other, why are they attracted by the − and + charges respectively on electrodes during electrolysis? or why, again, do the similarly charged atoms not attract each other (as dissimilarly charged ones are supposed to repel each other) and form hydrogen and chlorine molecules?

That a molecule, when decomposed by some force superior to the attraction of its constituent atoms, gives rise to free atoms which are possessed of a certain amount of free energy, and that this free energy, which we call chemical affinity, may really be of the nature of an electric charge, has received the support of the greatest chemists and physicists whom Science has known; but the present theory seems to have nothing in common with such a view—indeed, it seems to be directly opposed to it. On the old theory the atoms when separated have *more* free energy than when combined, on the new theory they have *less*: on the old, the electric charges are the *consequence* of decomposition by some superior force, and form an integral part of the stuff resulting from the decomposition; on the new, they are the *cause* of this decomposition and are something outside and independent of the matter itself. The old theory attributes chemical affinity and combination to the existence of these charges; the new theory considers the charges to be antagonistic to chemical affinity, and to be the cause of chemical decomposition.

The view has been suggested, I believe, that the supposed

dissociated atoms, though no longer held together by chemical attraction, may be still held together by the electrical attraction of their charges. This seems to be but an attempt to overcome a difficulty by changing a name, and so far from really diminishing the difficulty, it would appear only to increase it: for heat has been evolved, and, therefore, the state of combination is more intimate than it was before dissolution, so that the matter must be held more firmly together by these electrical charges than it was by its chemical affinity: how does this help the statement that they are *less* firmly united now—so much less firmly according to the theory, that they act as independent units? The difficulties as to the origin of the charges and the antagonism of chemical and electrical attraction are, moreover, not removed by this method of expressing the theory.

Another view, again, was suggested at the recent meeting of the British Association: that, instead of regarding the ions as atoms with electric charges, they might be regarded as allotropic modifications of the atoms themselves. This appears to me to be but hypothecating a new form of matter to satisfy a theory which is inconsistent with known matter, and, inasmuch as atoms of the same substance cannot differ from each other except by possessing different quantities of energy, it practically amounts to the conjuring away a stock of energy that the theory may not be said to be contradicted by the principle of the conservation of energy. But surely such a process is in reality as much a violation of this principle as writing $2=4$ would be. The energy equation will not equate, so the excess of energy on the one side is boldly struck off by imagining a new form of energyless atom, just as on the electric-charge theory the same is done by saying that the superabundant energy has been expended in combining with charges which have come from nowhere.

Whereas the potential energy of the ions of a substance such as hydrochloric acid must be regarded as less than that of the molecules when gaseous, it would appear that it must be greater than that of the molecules when solid—at any rate in such cases where the solid dissolves with an absorption of heat. Thus, in the case of potassium chloride, 74·5 grams of the salt dissolve in water at 0° with an absorption of 5184 cal. Let P and K represent the potential and kinetic energy of the solid (KCl) and of the ions (K + Cl) respectively, then

$$\mathrm{P(KCl)+K(KCl)=P(K+Cl)+K(K+Cl)-5284\ cal.}$$

The kinetic energy of the solid, K(KCl), is possibly an unknown quantity, but it is certainly a positive quantity; the

kinetic energy of the dissolved substance, K(K + Cl), can, according to the osmotic-pressure theory, be calculated. With a monatomic gas no intramolecular work is possible, and therefore the pressure caused by that gas is a measure of its total kinetic energy (*cf.* Ostwald, *loc. cit.* p. 76); the pressure of each ion is in this case, *ex. hyp.*, the same as that which an ordinary molecule produces, and the pressure-producing energy of a gram-molecular proportion of such a gas is 34,008,000,000 ergs, or 819 cal., so that

$$K(K + Cl) = 2 \times 819 \text{ cal.},$$

$$\text{and } P(KCl) = P(K + Cl) - 3646 \text{ cal.} - K(KCl);$$

thus the potential energy of the ions must be considerably greater than that of the solid molecule.

The same substance might have been taken as an instance of a gas dissolving with evolution of heat and a solid with absorption of heat; and in such a case the potential energy of the substance in solution must be intermediate between that of the gaseous and solid molecules. It is certainly difficult to imagine that this substance can consist of uncombined atoms.

But a still greater difficulty arises in some cases: a solution of calcium nitrate, for instance, absorbs heat on dilution, and, as the only change produced by diluting an already dilute solution is, according to the theory, to dissociate into ions some of the molecules still remaining intact, and as these molecules are present in the uncombined and gaseous condition, it follows that the dissociation of gaseous calcium nitrate molecules must absorb heat; therefore the gaseous salt on being dissolved in excess of water must absorb heat, the liquid salt would absorb more than the gas (by an amount equivalent to the heat of vaporization of this salt), and still more would be absorbed by the solid; yet direct experiment shows that this last, instead of giving a large absorption, actually *evolves* 4000 cal. when it is dissolved.

The conception that salts &c. in solution are entirely decomposed into ions has been regarded as a development of the theory of Clausius that a few free ions exist at any given moment in a mass of solution. But these two views appear to me to be radically different. Clausius's conception (Phil. Mag. 1858, vol. xv. p. 100) was of a two-fold nature. (1) That the molecules in any fluid, being at different temperatures at different times, owing to the impacts to which they have been subjected, some of them may occasionally be so hot as to be above their dissociation temperature, and that some temporarily free atoms would therefore be present. (2) That two similar molecules

MR and M′R′ might collide under such circumstances that M′ might come nearer to R than M was, and, consequently, M′R would be the result; whether, however, M and R′ would find themselves in such close proximity that they would instantly combine together, or whether they might remain for a time actually free, is a question which our ignorance of the distances and forces concerned do not allow us to settle. Williamson's theory (Phil. Mag.) was practically identical with Clausius's second proposition—continual interchange of radicals, but not necessarily the presence of free atoms. Clausius's theory was proposed to account for the facts of Electrolysis, Williamson's to account for Chemical facts. Nothing which has come to light since that time seems to have shaken the idea of a continual interchange of atoms in the molecules of a liquid; there seem, however, to be decided objections to the conception of free atoms being present. Whether it is probable that in a liquid at ordinary temperatures there can be any molecules as hot as the dissociation temperature (which is probably 1000° to 2000°) or not, is a matter of opinion; but if any free atoms are present the chances of their meeting atoms of the same nature would be equal to those of their meeting atoms of the opposite nature: with the former they would combine just as they do with the latter, and the result would be that hydrogen and chlorine gas would be formed, and the acid would gradually become entirely decomposed: nor can it be argued that the similar charges on the free atoms of the same substance would prevent these combining, for in the analogous case of hydriodic acid we know as a fact that free iodine is produced when the acid is heated to its dissociation temperature.

It does not seem necessary, however, to imagine the presence of free atoms to explain the phenomena of electrolysis (*cf.* Lodge, B. A. Report, 1887, p. 338). The facts of the case, I believe, are that although an E.M.F. of finite magnitude is required to produce sensible electrolysis, *i. e.* the liberation of gas, &c. in recognizable quantities, any electromotive force will produce results indicative of electrolysis, these results being a gradual leakage of electricity, and a reverse or polarization current on removing the battery. The leakage may be explained by the electrolysis of those molecules which happen to be at a temperature above that of the average molecule, and decomposable by a lower E.M.F. than is the average molecule, or else by the action of the E.M.F. on those dissimilar atoms which at the moment when they lose their original partners find themselves comparatively very far apart from each other (M and R′ in the case above cited). As to

the polarization current I venture, though with considerable diffidence, to ask whether it really is evidence of actual electrolysis. It is explained by the statement that a coating of liberated ions is formed on the electrode, and that these cannot be discharged so as to become ordinary atoms till the potential of the electrode attains a certain value, they consequently remain there and cause a reverse current. But might not such a current be caused by a similar coating of simple but undecomposed molecules; such molecules are, I believe, not fully saturated compounds, but still possess a certain amount of residual affinity, or, on the older electrochemical theory, a certain amount of unneutralized charge; these would be attracted to the electrodes and would present their + and − ends to the − and + electrodes respectively: a charge would thus be retained on the electrodes after the battery was disconnected, and this charge would cause a reverse current when the two electrodes were connected together. The action in fact would be similar to that in a condenser. Such an explanation may obviate objections which can, perhaps, be urged against the idea of a coating of ions, for it seems difficult to see why a certain E.M.F. should be reached before the atoms can discharge themselves, unless we imagine a definite attraction between an atom and its charge, or why the E.M.F. required to effect this discharge should not always be the same whenever the same element is liberated; it also obviates the necessity of regarding an ion as possessing any form of charge which a free atom does not.

Whatever be the value of these suggestions, and of the objections raised against that part of Clausius's conception which supposes the presence of a *few* free atoms in a liquid owing to the accidental superheating of some of the molecules, it must be borne in mind that this view is totally distinct from the modern dissociation theory, that *all* the molecules are dissociated, and that too not by heat but by their affinity for electrical charges of incredible origin, and possessing hitherto unknown characteristics.

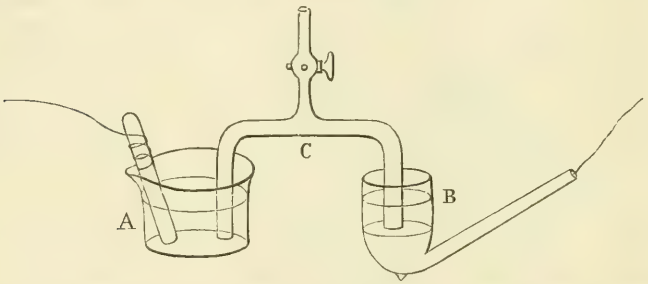
IV. *On Changes of Voltaic Energy of Alloys during Fusion.* *By* Dr. G. Gore, *F.R.S.**

M. J. REGNAULD has observed that liquid gallium is electropositive to solid gallium in a neutral solution of gallous sulphate (*Comptes Rendus Acad. Sci.* June 10, 1878; 'Chemical News,' vol. xxxviii. p. 33). He states that

* Communicated by the Author.

this "categorical experiment renders manifest, in a very simple case, the influence exercised by the heat of constitution upon the energy of its chemical properties;" and that "the available chemical work which a body possesses depends not only upon the specific nature of the atoms, but also upon the total of calories which its maintenance in the physical state determines."

The object in making the following experiments was to ascertain whether, consistently with the above observation, the change of physical state of an alloy from solid to liquid by fusion, and the large absorption of heat which then occurs, is usually attended by a correspondingly large increase of voltaic electromotive force, and whether the converse effect occurs during solidification. The apparatus employed in the experiments is shown by the annexed sketch.



A is a glass cup, B a tobacco-pipe with a wide bowl, and C a bent glass syphon-tube provided with a tap. A bar of the alloy was placed vertically in A, and a second portion of the alloy was melted in the bowl and some distance up the stem of the pipe B, so as to exclude the production of thermo-electric currents at the junction with the connecting wire, and then allowed to solidify and cool.

The electrolyte, at atmospheric temperature, was poured into A and B, and a portion raised by suction into C so as to connect the portions in A and B. The terminals of the portions of alloy were connected by iron wires with a suitable astatic galvanometer of 100 ohms resistance, and the needles allowed to settle at zero. Heat was then gradually applied by means of a small flame to the bowl of B until the alloy in it melted, and the temperature of the electrolyte was raised nearly to the boiling-point; the flame was then removed. The amounts of deflexion of the needles of the galvanometer at definite intervals of time, during the heating and cooling, and especially at the fusing and solidifying points, were carefully observed and recorded.

Three electrolytes were used, viz. one composed of 1 part by weight of absolute hydrochloric acid in 100 of water; a second, of 1 part of chloride of sodium and 100 of water; and a nearly saturated solution of that salt.

In the following experiments: 1st, on applying heat, the heated portion of the alloy became gradually electropositive to the cold portion up to its fusion-point; and, 2nd, a more or less sudden increase of electromotive force occurred during the further heating of the alloy and the electrolyte up to the boiling-point of the latter, and this sudden increase appeared to coincide in point of time with the melting of the alloy, but this could not be accurately determined, especially with the amalgams in experiments No. 4, 5, and 6, because the fusion-point was not sufficiently sudden or distinct. Substantially the reverse of these phenomena happened after removing the flame, during the processes of evolving latent heat and subsequent cooling. A partial exception to the phenomenon of sudden increase of electromotive force during the act of fusion took place with cadmium amalgam in experiment No. 7.

Experiment 1. Fusible alloy of bismuth 70 parts, lead 40, tin 20, and cadmium 15. Melting at about 66° C. In the dilute acid at 16° C. The amount of sudden effect by gradual heating in this case was quite large, and the galvanometer deflexion increased from 20° to 60°. *Experiment* 2. The same alloy in the weak solution of sodium chloride at about 16° C. The amount of sudden increase of current by gradual heating was again large. *Experiment* 3. An alloy of bismuth 8 parts, lead 8 parts, and tin 3. Melting at about 107° C. In the concentrated solution of sodium chloride. The sudden increase of current by gradual heating was considerable.

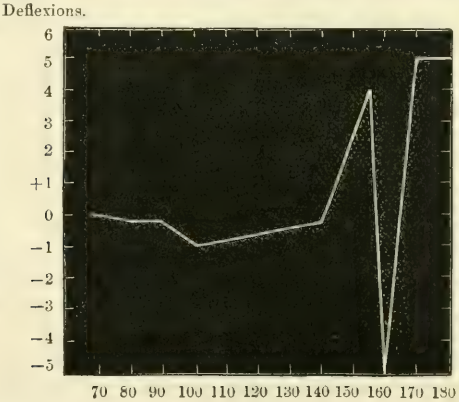
As in each of these instances there was a more or less sudden change of physical state of the alloy, but no such change of the electrolyte, the coincident rapid increase of electromotive force must have been due to the alloy and not to the electrolyte; it could not have been due to a sudden rise of temperature, because that of both substances must have remained nearly stationary during the act of fusion in consequence of the heat becoming latent.

The next three experiments were made with mercurial amalgams. *Experiment* 4. An amalgam of bismuth 10 parts, tin 3·5, lead 3·2, and mercury 2·0, in the weak solution of common salt. *Experiment* 5. Amalgam of zinc 1 part, and mercury 7, in the same liquid. *Experiment* 6. Amalgam of tin corresponding in composition to the formula Sn_4Hg_5, in the same solution. This amalgam was soft at 16° C., and mercury drained out of it after standing a bar of it some

time in a vertical position. Each of these amalgams gave only a small amount of sudden increase of current at the period of liquefaction, probably because the liquefaction was more gradual, and the effects of solution in mercury of the other metals present masked those of fusion.

Experiment 7. An amalgam of 1 part cadmium and 4 parts of mercury, in the weak solution of common salt. The amalgam was more solid at 16° C. than the other three, but it easily liquefied in boiling water. When it was heated and had become pasty, the current began to increase; but just previous to complete liquefaction the current suddenly and considerably decreased, and the liquid amalgam became electro-negative to the solid one; the period of reversal was very brief, and on further heating the current suddenly increased to a slightly higher point than it was at previously. The annexed curve approximately represents the results obtained with a freshly prepared portion of the amalgam, and shows that the phenomenon is much more complex than a simple measurement of the total amount of heat evolved or absorbed would indicate. The sudden depression of electric energy was probably due to a sudden act of chemical union of the ingredients and a corresponding loss of potential (*i. e.* latent or specific) heat.

Curve of Variation of Electromotive Force of Cadmium Amalgam produced by heating and fusion in a 1-per-cent. Solution of Sodium Chloride.



Above 0 the hot electrode was +, below 0 it was negative to the cold one.

By repeated experiments of the above kind with this amalgam it was found that the sudden decrease of electric current was greater with the freshly prepared substance than with that which had been remelted several times, and 1

have examined this interesting circumstance (see "Changes of Property of Amalgams by Repeated Fusion," Phil. Mag. September 1890, p. 228).

The mixtures of metals which produced the most sudden increases of current in these experiments were those which exhibited the most sudden liquefaction. An explanation I venture to suggest of the increase of voltaic energy during liquefaction is, that the molecules of the liquefied alloy are usually in a state of more active motion than those of the solid substance, partly because the liquid has absorbed more potential heat; and that the suddenness of the increase of the current at the period of liquefaction is due to absorption of heat being promoted, and chemical and voltaic action facilitated by the sudden occurrence of convection currents in the liquid alloy.

As energy is indestructible, the effect of each unit of heat absorbed by the alloy upon its total amount of energy of molecular motion must be the same whether the heat is absorbed as specific heat and raises its temperature, or as latent heat which, without altering its temperature, changes its physical state by fusion, or its other properties, as in the case of iron at its "critical point."

The results of the experiments show that changes of voltaic energy may be used in the above manner to detect physical and chemical changes in metallic alloys.

V. *A Kinetic Theory of Solids, with an Experimental Introduction.* *By* William Sutherland *.

THE present work started in an experimental inquiry having a twofold object,—to try to ascertain whether there is a general law connecting the elastic properties of metals with temperature, as is the case with gases, and to discover it if possible, and, failing that, to obtain empirical means of finding the values of the elastic constants of the metals at absolute zero, at which temperature they would be specially interesting, as the molecules would be at rest.

The first result was that a general law unfolded itself with singular ease, namely that the law of variation of the rigidity of the metals with temperature is the same for all: if n is the rigidity at absolute temperature θ, and N that at absolute zero, while T is the melting-point, then

$$\frac{n}{\mathrm{N}} = 1 - \left(\frac{\theta}{\mathrm{T}}\right)^2,$$

a law almost as simple as that of perfect gases.

* Communicated by the Author.

It next appeared in a similar manner that the law of variation of Young's modulus of elasticity with temperature is nearly the same for all metals, and nearly, though not quite, as simple as that for rigidity.

As these results amounted to an experimental proof that rigidity (and elasticity generally) is essentially a kinetic phenomenon I was encouraged to proceed with a kinetic theory of solids, which had been in view when the experimental inquiry was undertaken.

The present paper will be divided into two parts :— Experimental Introduction and Theory.

Experimental Introduction.

This will be divided into two parts, Rigidity and Young's Modulus, in which the matter will be taken in the following order :—first, an account of my own experiments on the effect of temperature on elasticity ; second, a compilation of all available data on the same subject ; third, a compilation of all the available data as to the absolute values of Rigidity and Young's Modulus at about 15° C. ; and fourth, establishment of the general law connecting these elastic constants with temperature, and determination of their values at absolute zero.

Rigidity.

1. *Experiments.*—The variation of rigidity with temperature has been worked at by Napiersky, Kohlrausch, Pisati, and Tomlinson ; but these experimenters have almost confined their attention to the nobler metals with high melting-points. As I expected that in the case of the metals with low melting-points the law of variation would be easier to discover, it was necessary to make a study of these metals.

I used the torsional method of measuring rigidity both in its static and kinetic form, and found the two forms to give agreeing results ; but as the static proved less accurate, I will not waste space by giving its results here. The kinetic method was worked in the usual manner. The metal to be experimented on was taken in the form of a wire, with a cylindrical vibrator of thin sheet iron soldered to one end, and a strip of thin iron to the other by means of which it could be clamped. As chamber in which to produce variations of temperature, a wooden box about 65 centim. by 20 by 27 was taken and fixed with its long edge vertical. The top and bottom had a hole bored at each middle point to let the wire pass through freely. The iron strip was clamped to the top of the box, and the vibrator either swung just outside or inside

the box according to the length of the wire. It was convenient to have the vibrator swinging outside when it was necessary to largely increase the moment of inertia of the vibrator. To heat the chamber I used as a preliminary expedient a gas-flame burning inside it at one of the bottom corners with vent-holes so distributed as to prevent the concentration of a stream of hot air on any one point of the wire. The mean temperature of the chamber could be regulated by the size of the flame, and was measured by a thermometer the bulb of which was almost in contact with the middle point of the wire. Although this was intended to give only rough preliminary measurements, it worked so well and was so simple and handy that I retained it throughout. It was tested repeatedly in the following manner :—a gas-flame was turned on sufficient to maintain a constant temperature of say 70° C., as recorded by the thermometer, and the period of vibration of the wire under experiment was observed. The flame was then increased till a temperature of 105° C. was reached, when the flame was turned off, and the vent-holes closed ; the temperature of the chamber then fell slowly and the period of vibration of the wire was again observed while the temperature fell from 71° to 69° ; the difference in the two values of the period never amounted to more than what would correspond to an uncertainty of 2° in the reading of the temperature, and in most cases was actually inappreciable. This was a degree of accuracy quite sufficient for the purpose in view.

In determining the period of vibration of wires with such molecular viscosity as those of lead, tin, and zinc, there is this difficulty, that when vibration is started it tends to die away after a very few swings, so that accuracy in the measurement of the time of a single swing is not possible without some method of periodically reinforcing the swing. I found the simplest and best plan of doing this to be the application of a slight impulsive couple with the hands to the vibrator at the middle of every nth swing. With a little practice it was soon possible to make a large number of measurements of the period of a lead wire not differing amongst themselves by more than 1 in 300. Each determination of a period of vibration was made by observing with the seconds hand of a watch the time of between 100 and 300 swings.

The rigidity is calculated from the experimental data by the formula

$$n = \frac{2\pi^3 \mathrm{I} l^3 \rho^2}{m^2 (t/2)^2},$$

n being the rigidity, l the length of the wire vibrated, m its mass, ρ its density, I the moment of inertia of the vibrator, and t the time of a complete vibration. Using C.G.S. units in the measurements, the rigidity is given in dynes per square centim., but as the gramme weight is the unit of force most employed by elasticians it will be used here.

When the vibrator swung outside the chamber, a small length of the wire was not heated directly but only by conduction; to allow for this the small length was assumed to be at the temperature of the external air. Let n_1 be the rigidity at the initial temperature θ_1 of the surrounding air, n_2 that at any higher temperature θ_2, and λ the length of the small part of wire outside of the chamber, α the coefficient of linear expansion of the wire, t_1 and t_2 the periods observed at the two temperatures, then the ratio n_2/n_1 is given by the formula

$$\frac{n_2}{n_1} = \frac{l-\lambda}{l}\,\frac{1}{1+3\alpha(\theta_2-\theta_1)} \div \left[\left(\frac{t_2}{t_1}\right)^2 - \frac{l-\lambda}{l\{1+\alpha(\theta_2-\theta_1)\}}\right].$$

Lead.—Commercial wire.

l.	λ.	m.	ρ.	I.
77·05 cm.	4 cm.	28·4 gm.	11·4	586500 gm. cm.^{2}

Temperature C. θ	21°	60°	102°
Half-period $t/2$	5·51 sec.	5·71	6·00
Rigidity ratio n_2/n_1	1·00	·924	·829

Rigidity at 21° C., 90×10^6 grammes weight per sq. cm.

To control the absolute value found, a large number of measurements were made on a longer wire with a lighter vibrator; length 238·7 centim., mass 88 gm., density 11·4, moment of inertia of vibrator 3350 gm. centim.^{2}, temperature 17° C., and half-period ·7365 sec. These values give a rigidity 90×10^6 at 17° C., in close agreement with the value found from the shorter wire.

To make still surer of getting this absolute value of the rigidity of lead thoroughly tested, I carried out some experiments on a much larger scale, using a piece of stout lead pipe instead of wire. For vibrator a rectangular plank 179·7 centim. long and 14·6 centim. wide was taken; a hole was bored at its centre through which the pipe was pushed till a short length projected which was slit and hammered back in four flaps, then strongly nailed to the plank; a conical plug being driven into the pipe, there was no doubt about the rigidity of the connexion between pipe and vibrator. The plank weighed

2649 gm. The other end of the pipe was similarly secured to a plank which was clamped as rigidly as possible to the beams of a roof. In the case of a hollow cylinder of external radius r_2 and internal radius r_1 rigidity is given by the formula

$$n = \frac{8\pi^2 \mathrm{I} l^2 \rho}{t^2 m (r_2^2 + r_1^2)}.$$

The moment of inertia of the plank could be increased by adding weights.

l.	m.	ρ.	θ.	r_2.	r_1.
120·9 cm.	1699 gm.	11·4	23°	·9014 cm.	·6482 cm.

With the plank alone, whose moment of inertia was 7176000 gm. cm.^{2}, the period was ·717 sec. ; the moment being increased to 10577000 the period became ·881 sec., and with the moment again increased to 20684000 the period rose to 1·222 sec. These values give for the rigidity the values $89{\cdot}3 \times 10^6$, $87{\cdot}2 \times 10^6$, and $88{\cdot}6 \times 10^6$ respectively, the differences being due doubtless to imperfect rigidity in the supporting of so heavy a vibrating system. The mean value $88{\cdot}4 \times 10^6$ at 23° is close enough to the former value 90×10^6 at 17° to make it pretty certain that the absolute value of the rigidity of lead at 20° can differ but little from 89×10^6 grammes weight per sq. centim.

Zinc.—To get a wire of zinc I had a strip about ·3 centim. wide cut from a sheet of rolled zinc ·3 centim. thick. The rod of square section was then roughly trimmed to circular section with a file, and, finally, by longitudinal scraping while kept revolving it was converted into a fairly uniform circular wire.

l.	λ.	m.	ρ.	I.
73·7	5·1	36·3	7·04	586500

θ C....	18°	48°	63°	82°	97°	67°	52°	21°
$t/2$ ...	1·338	1·367	1·398	1·446	1·495	1·405	1·382	1·340
n_2/n_1,	1·0	·952	·906	·842	·784	·897	·930	·997

Rigidity at 18°, 311×10^6 grammes weight per sq. centim.

Tin.—Again I had to make a wire, this time by casting a rod and hammering out to three times its original length. I did not succeed in getting uniformity or true circularity of section, so that a reliable absolute value of the rigidity of tin is not obtainable from these experiments, but the rigidity ratio being independent of the form can be accurately got.

l.	λ.	m.	ρ.	I.	
71·7	2·5	37·45	7·29	586500	
θ C.....	16°	51°	66°	86°	103°
$t/2$	2·15	2·35	2·42	2·54	2·65
n_2/n_1.....	1·0	·854	·804	·727	·666

The rigidity at 16° is 109×10^6, an uncertain value.

To get a more accurate absolute value of the rigidity of tin, I carried out some experiments on a large scale on a piece of tin pipe in the same manner as on the lead pipe.

l.	m.	ρ.	θ.	r_2.	r_1.
116·8	795·5	7·29	18°	·689	·429

With the three moments of inertia 7176000, 10577000, and 20684000 the periods were ·851, 1·029, and 1·418 sec., and the corresponding values of the rigidity are $154{\cdot}3 \times 10^6$, $156{\cdot}1 \times 10^6$, and $160{\cdot}9 \times 10^6$; the mean rigidity of tin at 18° being therefore 157×10^6. This is a more reliable determination than the last.

Magnesium.—The specimen used was a piece of commercial fine wire.

l.	λ.	m.	ρ.	I.
54·6	0	·25 gm.	1·74	525 gm. cm.^{2}
θ	21°	100°		
$t/2$	1·42	1·45		
n_2/n_1	1·0	·955		

Rigidity at 21°, 130×10^6.

To check this value of the absolute rigidity another determination was made on a longer wire with a heavier vibrator; l 200·6, m ·891, ρ 1·74, I 3395, θ 21°, $t/2$ 7·10. Rigidity 131×10^6, a result in good agreement with the last.

2. *Compilation of Data as to Variation of Rigidity with Temperature.*—The most extensive work yet done on this subject is that of Pisati (Wied. *Beibl.* i.), who studied silver, copper, gold, aluminium, iron, steel, and platinum from zero to 200°, and in some unannealed specimens up to 300°; but the results at high temperatures on unannealed specimens are of no use for our present purpose, because mixed up with the pure temperature effect there is an annealing effect. However, from zero up to 100° the proportional change of rigidity of the metals with high melting-point is nearly the same in the unannealed as in the annealed state. The other sources

of knowledge on this subject are Kohlrausch and Loomis (Pogg. *Ann.* cxli.), Napiersky (Pogg. *Ann.*, *Erganzbd.* iii.), and Tomlinson (Proc. Roy. Soc. xl.), who do not go beyond 100°. The simplest way of comparing the results of different experimenters will be to tabulate the ratio of the rigidity at 100° to that at zero as found by each. I will also give from Pisati the ratio for rigidity at 200°. Where a specimen is known to have been unannealed it will be marked (*u.*)

TABLE I.

Metal.	100°.	200°.	Authority.
Copper (*u*)	·969	·911	Pisati.
Copper	·971	·917	Pisati.
,,	·945		Kohlrausch.
,,	·971		Tomlinson.
Silver (*u*)	·960	·858	Pisati.
Silver	·956	·898	Pisati.
,,	·962		Napiersky.
,,	·961		Tomlinson.
Gold (*u*)	·971	·912	Pisati.
Magnesium	·943		Sutherland.
Zinc	·843		Tomlinson.
,,	·749		Sutherland.
Aluminium (*u*)	·932	·803	Pisati.
,,	·943		Tomlinson.
Tin	·638		Sutherland.
Lead	·773		Sutherland.
Iron	·979	·942	Pisati.
,,	·960		Napiersky.
,,	·950		Kohlrausch and Loomis.
,,	·973		Tomlinson.
Nickel	·974		Tomlinson.
Platinum (*u*)	·984	·964	Pisati.
Platinum	·982	·934	Pisati.
,,	·993		Tomlinson.

The discrepancies in the above table are such as have hitherto proved inevitable in elastic experiments on account of differences in purity of specimen and elastic state. But in Pisati's experiments up to 200 for the metals with high melting-point, and in my own up to 100° for those with low melting-point, there is a large enough variation of rigidity to be only slightly perturbed by accidental circumstances, as will be seen when the law of variation is under discussion. In the case of zinc, where there is pronounced disagreement between Tomlinson's result and my own, Tomlinson's is to be preferred as he experimented on a true wire.

3. *Compilation of Data as to Absolute Values of Rigidity at Ordinary Temperatures* (between 0° and 20°).

The sources of these data are, in addition to those mentioned in the last compilation, Kupffer (*Mém. de l'Acad. des Sc. de St. Pét.* 6 sér. t. v.), Tomlinson (Phil. Trans. 1883, and Proc. Roy. Soc. xlii.), Sir W. Thomson (*Encyc. Brit.* art. Elasticity), and Kiewiet (Wied. *Ann.* xxix.).

The rigidity is given in grammes weight per square centimetre.

TABLE II.

Metal.	$n/10^6$.	Authority.	Metal.	n 10^6.	Authority.
Copper	390	Kohlrausch and Loomis.	Aluminium (u)	234	Pisati.
				250	Tomlinson.
	397	Pisati.		267	Tomlinson.
	441	Tomlinson.		241	Thomson.
	420	Tomlinson.	Tin	121	Tomlinson.
	457	Tomlinson.		150	Kiewiet.
(mean of many)	449	Thomson.	(hammered)	109	Sutherland.
	440	Kiewiet.	(pipe).....	157	Sutherland.
Copper (u).....	436	Pisati.	Lead	74	Tomlinson.
Silver	283	Kupffer.		89	Sutherland.
	257	Pisati.		88	Sutherland.
	272	Tomlinson.	Iron	742	Kupffer.
	270	Thomson.		713	Kupffer.
Silver (u)	331	Pisati.		694	Kohlrausch.
Silver (u)	276	Tomlinson.		811	Pisati.
Gold	271	Kupffer.		773	Tomlinson.
	281	Thomson.		751	Tomlinson.
Gold (u)...	265	Pisati.		766	Tomlinson.
Magnesium ...	172	Tomlinson.		790	Thomson.
	130	Sutherland.	Nickel.....	758	Tomlinson.
Zinc (u)	340	Tomlinson.	Platinum	637	Kupffer.
	360	Thomson.		628	Pisati.
	380	Kiewiet.		693	Tomlinson.
Zinc (rolled anneal.)	311	Sutherland.		662	Tomlinson.
				622	Thomson.

The discrepancies in this table must be due mainly to differences in purity and elastic state. But on taking the mean of the above values for each element we must obtain values near to the true ones at 15°; these are now given.

TABLE III.

Mean values of 10^{-6} times the Rigidity at 15° C.

Cu.	Ag.	Au.	Mg.	Zn.	Al.	Sn.	Pb.	Fe.	Ni.	Pt.
430	280	270	150	350	250	135	84	750	760	650

4. *General Law of the Variation of Rigidity with Temperature.* The method of procedure in discovering this law was as follows:—For no single metal was the temperature range large enough to show clearly any simple law, but if the molecules of the different metals behave like similar dynamical systems, then, in passing from the rigidity of rest at absolute zero to the vanishing point of rigidity at the melting-point, the different systems must show close similarity in behaviour. The first thing to do, then, was to find some empirical formula with which to extrapolate for a first approximation to the rigidity at absolute zero. In addition to the experimental data, there was the valuable fact that in each case the rigidity is known to vanish at the known melting-point, so that, although only a small arc of the whole curve of rigidity and temperature was known in each case, the curve could be pretty safely completed by sentiment down to the point of zero rigidity at the melting-point. The curves thus drawn looked as though they could be fairly represented by the empirical formula

$$\frac{1}{n} = a + b\,10^{\frac{c\theta}{T-\theta}},$$

T being the melting-point. This makes the rigidity vanish at the melting-point, and allows the three constants a, b, c to be determined from three values of the rigidity at different temperatures: the formula therefore represented a large stretch of curve, and could with some confidence be used for extrapolating over about 300° down to absolute zero. In this manner a preliminary series of values of N, the rigidity at absolute zero of the various metals, was found. Then it was possible to express the value of the rigidity of each metal at all temperatures in terms of the value at absolute zero as unit, and, further, it was promising to express temperature for each metal in terms of its melting-point as unit. When the rigidity ratios so found for the different metals were plotted as ordinates to the temperature ratios as abscissæ, the points for all the metals were found to lie on one curve, a parabola with the equation

$$\frac{n}{N} = 1 - \left(\frac{\theta}{T}\right)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The temporary exponential form can now be discarded; and we will proceed at once to the proof that the simple relation just given is the actual law of the variation of rigidity with temperature. The best way to proceed with the data

already given in this paper will be as before to measure rigidity for each metal in terms of that at common temperatures (about 15°) as unity, and then according to the data given in the earlier part of this paper for lead, zinc, tin, and magnesium, and in Table I., after Pisati, to calculate a value of N/n_1 from equation (1) for each value of n given for the different values of θ.

For example, in the case of tin we have the following values, T=503° (absolute):—

θ...	289°	324°	339°	359°	376°
n_2/n_1...	1·0	·854	·804	·727	·666

which give respectively the following values of N/n_1:—

1·492 1·461 1·472 1·480 1·510,

with a mean value 1·483, the departures from which are within the limits of experimental error.

In the case of zinc, as already mentioned, there is discrepancy between Tomlinson's results and my own; Tomlinson gives for the rigidity of zinc at any temperature the formula

$$n_t = n_o\,(1 - ·00108t - ·0000049t^2),$$

by means of which I have calculated the rigidities at the same temperatures as my own determinations were made at in terms of that at 18° as unit in the following, T=690°:—

θ	291°	321°	336°	355°	370°
n_2/n_1 (Toml.)	1·0	·955	·932	·896	·865

These give the following values of N/n_1:—

1·217 1·218 1·221 1·218 1·215;

while at the same temperatures my own experiments give

n_2/n_1	1·0	·952	·906	·842	·784
N/n_1	1·217	1·215	1·188	1·145	1·101

Thus, while Tomlinson's values confirm the formula with wonderful accuracy, my own fail to do so, the reason being I believe that my specimen of zinc was not a genuine wire, whereas Tomlinson worked with a properly drawn wire; the mean value of N from his experiments is 1·218, with a maximum departure in the individual experiments of ·25 per

cent., which I take to be a very satisfactory confirmation of the law.

The following table needs no explanation now.

TABLE IV.

Temperature θ		273°	373°	473°	
Copper	n_2/n_1	1·0	·971	·917	T=1330°.
	N/n_1	1·044	1·054	1·050	Mean 1·05.
Silver	n_2/n_1	1·0	·956	·898	T=1230°.
	N/n_1	1·052	1·053	1·054	Mean 1·053.
Gold.....	n_2/n_1	1·0	·971	·912	T=1310°.
	N/n_1	1·045	1·056	1·049	Mean 1·05.
Aluminium	n_2/n_1	1·0	·932	.....	T=1120°.
	N/n_1	1·063	1·047	.....	Mean 1·055.
Temperature θ		294°	333°	375°	
Lead	n_2/n_1	1·0	·924	·829	T=599°.
	N/n_1	1·318	1·338	1·364	Mean 1·34.
Temperature θ		294°	.....	373°	
Magnesium	n_2/n_1	1·0	.....	·955	T=1023°.
	N/n_1	1·090	.....	1·102	Mean 1·096.
Temperature θ		273°	373°	473°	
Platinum.....	n_2/n_1	1·0	·982	·934	T=2050°.
	N/n_1	1·018	1·016	(·987?)	Mean 1·017.

In the case of iron, if the absolute melting-point 2080, as given by Carnelley, is taken, and Pisati's measurements of rigidity used to calculate N/n_1, the agreement is not satisfactory ; thus

Temperature		273°	373°	473	573°
Iron	n_1/n_2	1·0	·979	·942	·904
	N/n_1	1·017	1·011	·993	·978

but if the melting-point is taken at 1650°, which is within the limit of some determinations, then the values of N come out

1·028 1·031 1·026 1·028

with a mean value 1·028 and a maximum departure of ·3 per cent.

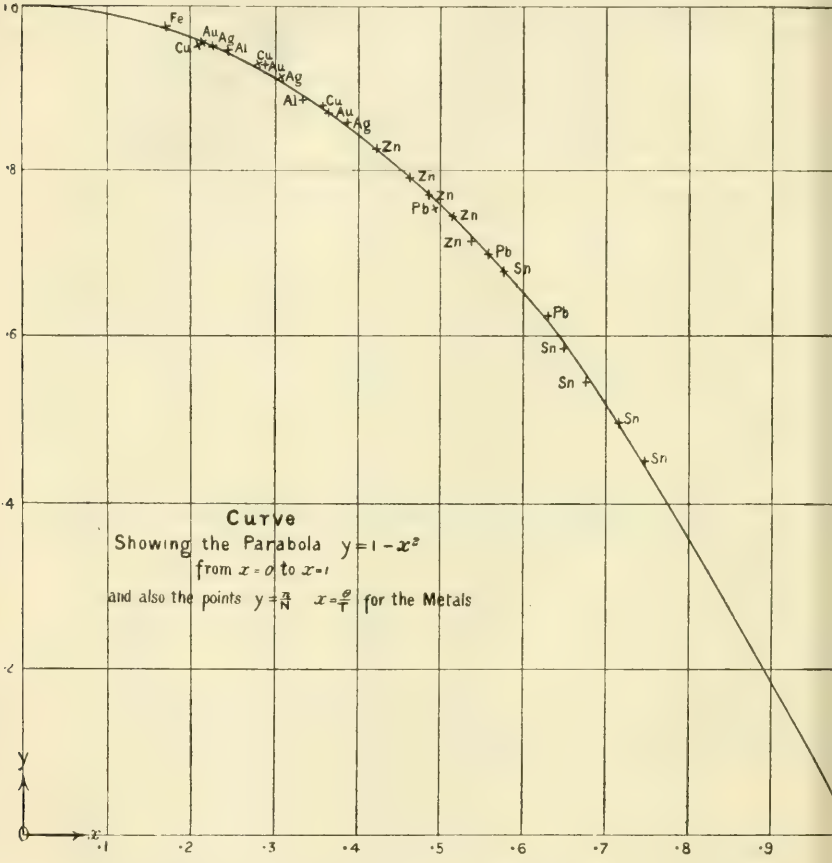
Using the mean values of N/n_1 just found, and the values of n_1 given in Table III., we get the following values of N :—

TABLE V.

10^{-6} N or 10^{-6} times the Rigidity at absolute Zero.

Cu.	Ag.	Au.	Mg.	Zn.	Al.	Sn.	Pb.	Fe.	Ni.	Pt.
452	295	284	164	426	264	200	118	771	781	661

The readiest way of clinching the whole demonstration now will be to draw the parabola $y=1-x^2$ from $x=0$ to $x=1$, and with the mean values of N/n_1 or N, calculating n/N as y and θ/T as x, to mark the separate points so determined. This is done in the figure.



For zinc Tomlinson's values of the rigidity are used, and for iron the melting-point is taken as 1650. To avoid excessive crowding of points on the figure all the points except one for iron, and all for platinum and magnesium are omitted. The course of the curve among the points proves that as regards the connexion between rigidity and melting-point the

molecules of the metals are similar dynamical systems, and also that

$$\frac{n}{N} = 1 - \left(\frac{\theta}{T}\right)^2.$$

This concludes the experimental inquiry as to rigidity. The result shows that rigidity in its essence is a kinetic phenomenon almost as simple in character as the elasticity of perfect gases.

[To be continued.]

VI. *Note on* Kohlrausch's *Theory of Ionic Velocity.* *By* W. C. Dampier Whetham, *B.A., Coutts Trotter Student of Trinity College, Cambridge* *.

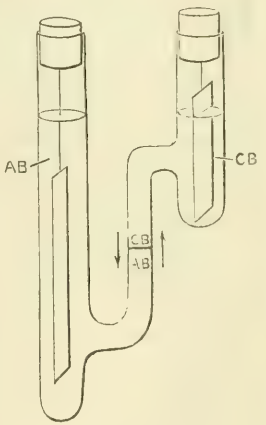
KOHLRAUSCH calculates his numbers for the specific velocities of different ions from measurements of the conductivities of salt-solutions, and of their migration constants, on the supposition that all the molecules of the salt present in solution are actively concerned in conveying the current. The values thus obtained were found to agree with experiment in certain cases by Prof. Oliver Lodge, and an investigation I am now engaged in carrying out seems also to confirm them. It seems to be generally supposed that this is inconsistent with any theory (such as that of dissociation) which supposes only a certain part of the salt to be active (see Lodge, B. A. Report, 1886, p. 391), though some such form of theory seems to be required by the relations shown to exist by Arrhenius, Van't Hoff, Ostwald, and others. If we examine the matter a little more closely, however, I think the two suppositions can be reconciled. Suppose that the ratio of the numbers of the active and the inactive molecules (which is generally supposed to measure the "dissociation") represents in reality the average ratio of the time during which each molecule is active to the time during which it is inactive. Every molecule is in turn active, but *at any instant* only a certain fraction of the molecules are active. [In terms of the dissociation hypothesis, the dissociation ratio measures the ratio of the mean free time to the mean paired time of the ions.] This is, of course, equivalent to supposing a certain fixed fraction of the whole number of molecules to be active, as far as statical effects, such as osmotic pressure, are concerned, but when we consider the velocities of the ions the case is different.

* Communicated by the Physical Society: read May 9, 1891.

Kohlrausch calculates the relative velocity of the two ions $U = u + v$ from the molecular conductivity k/m, where k = specific conductivity of the solution, and m its contents in gramme equivalents of salt, $U_1 = u + v = k/m$. If now we suppose that at any instant only $1/n$th of the number of molecules are active, we should apparently have to put $U_2 = \frac{kn}{m}$ *in order that the same current may be carried*, which would give $U_2 = nU_1$.

But this U_2 represents the actual velocity of the ions while they are "free," and if we take a "dynamical" view of the dissociation equilibrium, they are only free for $1/n$th of their time; while combined they have no relative velocity, and so their *average* velocity for any *long* time is $\frac{1}{n}U_2 = U_1$, the same as on Kohlrausch's hypothesis.

The investigation alluded to above, at which I am now working, seems to yield excellent results for certain cases, though it is of somewhat limited application. It consists in observing the phenomena at the junction of two salt-solutions, one of which is differently coloured to the other, when a current of electricity is passed across it. Salts are chosen which have one ion in common and the other different. Let us represent them by AB and CB, and consider the junction phenomena. The effect of the molecular interchanges will be a motion of B ions in one direction, and a motion of C ions and of A ions in the other. When a C ion crosses the boundary, it again forms CB, but the colour of CB is different to that of AB, hence the boundary between the colours will move.



The method will be discussed when more experimental results are obtained; it appears that by measuring the rate of this motion the velocity of the ions can be arrived at. The present is merely a preliminary communication in explanation of the experiments shown to the Physical Society of London on the occasion of their recent visit to Cambridge.

VII. *On the Solitary Wave.* *By* J. McCowan, *M.A., B.Sc., Assistant Lecturer on Natural Philosophy, University College, Dundee*.*

IN his Report on Waves to the British Association in 1844, Scott Russell gave an account of experiments he had made on the propagation, along the surface of still water in a straight channel with rectangular cross-section, of a wave consisting of a single elevation or depression, and which he called a wave of translation or solitary wave to distinguish it from waves forming part of a train. From these experiments he concluded that the solitary wave was unique, having characteristics entirely its own:—it had a definite form depending only on the depth and the volume of the water composing it, and this form, in the case of a wave of elevation, appeared to be propagated with constant velocity and without any change except such degradation in height as might reasonably be attributed to frictional and other disturbances.

In 1845 Earnshaw† sought to give a theory of these waves, but it was unsatisfactory as involving a discontinuity in the pressure within the liquid.

In his Report on Recent Researches on Hydrodynamics to the British Association in 1846, Stokes, commenting on Russell's experiments and Earnshaw's theory, concludes that the observed degradation of the wave is not to be attributed wholly, nor even chiefly, to friction, but is an essential characteristic of the motion; and, again, in 1847, in a paper "On the Theory of Oscillatory Waves"‡, he reiterates this opinion and offers a proof involving, however, an oversight which I shall be able to point out.

It has been thought by some that the solitary wave is included in the general theory of long waves, but this is certainly only so to a very rough approximation, for its velocity does not agree closely with that of the long wave, nor does it gradually increase in steepness in front as the long wave does, the change which does take place in it being simply a diminution in height and consequent increase in length such as might be caused by a dissipation of its energy by friction, &c.

The first sound approximate theory of the wave was given by Boussinesq in 1871§, who obtained an equation for its

* Communicated by the Author, having been read before the Edinburgh Mathematical Society, May 8, 1891.

† Trans. Camb. Phil. Soc. vol. viii.

‡ Trans. Camb. Phil. Soc. vol. viii.

§ *Comptes Rendus*, tom. lxxii.

form and the same velocity of propagation as Russell deduced from his experiments. In 1876 Lord Rayleigh* gave another method of approximation leading to an equation for the surface similar to that of Boussinesq and the same velocity of propagation. These theories, however, give little further information regarding the wave, and I am not aware that anything further has been done.

In the following paper I propose, after briefly discussing the general theory, to proceed to a somewhat detailed examination of the wave based on a simple but close approximation. It will be found that the results are in substantial agreement with Scott Russell's experiments, and confirm his opinion as to the unique character of the solitary wave of elevation.

It will be seen further that an approximate account of the phenomena of the breaking of waves on passing into shallower water follows naturally from the results obtained.

1. *General Theory of the Wave.*

Though the possibility of the propagation of a solitary wave without alteration in form and with constant velocity along a straight channel of rectangular cross-section has not been established on theoretical grounds, yet the result of experiment is such as to show that a method based on this assumption must lead at least to a highly approximate account of the motion. We shall assume, then, the invariability of the wave motion, understanding it of course to be two-dimensional, and shall in the first place suppose it reduced to steady motion by having impressed upon it a velocity equal and opposite to that of the wave propagation.

Take the axis of x in the horizontal bottom of the channel along the direction in which the wave is propagated, and that of z vertically upwards. Then noting that the motion is essentially irrotational as being propagated into (incompressible) liquid at rest, and putting therefore ϕ for the velocity potential and ψ for the current function, we must have $\psi + \iota\phi$ a function of $z + \iota x$. $(\iota = \sqrt{-1})$.

At a great distance from the wave the liquid will practically be at rest, and therefore in the corresponding steady motion it will be flowing uniformly: hence for the steady motion it is convenient to take

$$\psi + \iota\phi = -\mathrm{U}(z + \iota x) + f(z + \iota x), \quad . \quad . \quad . \quad (1)$$

where U is the velocity of propagation of the wave.

* Phil. Mag. April 1876.

To determine the form of $f(z+\iota x)$ we note that (i.) as the wave is to be solitary it must be non-periodic as regards x, (ii.) it must be finite and continuous throughout the liquid including the bounding surfaces, (iii.) when x is infinite (+or −) it must vanish or have a finite value independent of z or x, and (iv.) if we take $\psi=0$ at the bottom, it must be an odd function of $(z+\iota x)$.

Thus we obtain

$$f(z+\iota x)=\sum_{i=0}^{i=\infty} a_{2i+1}\tan^{2i+1}\tfrac{1}{2}m(z+\iota x), \quad . \quad . \quad . \quad (2)$$

with the restriction $mz<\pi$.

The condition for a free surface only remains to be satisfied, and for this the coefficients a_1, a_3 . . . may be determined by the method of successive approximation, but for the present at least we shall content ourselves with examining to what degree of accuracy this condition can be satisfied by taking the first term only.

2. *The First Approximation.*

Take, then,

$$\psi+\iota\phi=-\mathrm{U}(z+\iota x)+\mathrm{U}a\tan\tfrac{1}{2}m(z+\iota x), \quad . \quad . \quad (3)$$

which gives

$$\psi=-\mathrm{U}z+\mathrm{U}a\frac{\sin mz}{\cos mz+\cosh mx} \quad . \quad . \quad . \quad (4)$$

and

$$\phi=-\mathrm{U}x+\mathrm{U}a\frac{\sinh mx}{\cos mz+\cosh mx}. \quad . \quad . \quad . \quad (5)$$

Let q be the whole velocity and u, v its components parallel to the axes of x and z respectively, then

$$\frac{d.\psi+\iota\phi}{d.z+\iota x}=u+\iota v=-\mathrm{U}\{1-\tfrac{1}{2}ma\sec^2\tfrac{1}{2}m(z+\iota x)\}\ ; \quad . \quad (6)$$

which gives

$$u=-\mathrm{U}\left\{1-ma\frac{1+\cos mz\cosh mx}{(\cos mz+\cosh mx)^2}\right\}. \quad . \quad . \quad (7)$$

$$v=-\mathrm{U}\left\{1-ma\frac{\sin mz.\sinh mx}{(\cos mz+\cosh mx)^2}\right\}. \quad . \quad . \quad (8)$$

and

$$q^2=\mathrm{U}^2\left\{1+\frac{m^2a^2-2ma(1+\cos mz\cosh mx)}{(\cos mz+\cosh mx)^2}\right\} \quad . \quad (9)$$

By means of (4), (9) is immediately reducible to

$$q^2 = U^2 - 2mU(\psi + Uz)\cot mz + m^2(\psi + Uz)^2(\operatorname{cosec}^2 mz - 2/ma). \quad (10$$

Let h be the mean depth, or, which is the same thing, the depth at an infinite distance from the wave, then by (4) the value of ψ at the surface will be $-Uh$. Let η be the elevation of the surface above the mean level, then at the surface $\psi + Uz = U\eta$, and therefore by (4) the surface will be given by the equation

$$\eta = a\frac{\sin m(h+\eta)}{\cos m(h+\eta) + \cosh mx}; \quad . \quad . \quad . \quad (11)$$

and for the surface, (10) will reduce to

$$q^2 = U^2\{1 - 2m\eta\cot m(h+\eta) + m^2\eta^2(\operatorname{cosec}^2 m(h+\eta) - 2/ma). \quad (12)$$

So far the equations are exact. Now expanding (12) in powers of η and neglecting all beyond η^3 it becomes

$$q^2 = U^2\{1 - 2m\eta\cot mh + m^2\eta^2(3\operatorname{cosec}^2 mh - 2/ma) - 4m^3\eta^3\cot mh\operatorname{cosec}^2 mh + \&c.\}; \quad . \quad (13)$$

but for the free surface the condition to be satisfied is

$$q^2 = U^2 - 2g\eta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

So comparing (13) with this we see that if we take

$$mU^2\cot mh = g \text{ and } 3ma = 2\sin^2 mh$$

the motion under consideration will satisfy the condition for a free surface to that degree of approximation in which the term containing η^3 in (13) is considered negligible.

It is possible, however, to get at once a much closer approximation: for if we take $ma = \frac{2}{3}\sin^2 m(h + \frac{2}{3}\eta_0)$, where η_0 is a quantity of the same order of magnitude as η, (13) becomes

$$q^2 = U^2\{1 - 2m\eta\cot mh + 4m^3\eta^2(\eta_0 - \eta)\cot mh\operatorname{cosec}^2 mh\}, \quad (15)$$

and thus the condition (14) will be accurately satisfied (η^4 &c. neglected) where $\eta = \eta_0$ as well as of course where $\eta = 0$. Hence, for reasons which will be more fully examined immediately, we shall take for η_0 the maximum elevation of the wave or elevation of the crest above the mean level.

Thus, finally, taking

$$U^2 = gm^{-1}\tan mh \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and

$$ma = \tfrac{2}{3}\sin^2 m(h + \tfrac{2}{3}\eta_0), \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where, by (11),

$$\eta_0 = a\tan\tfrac{1}{2}m(h + \eta_0), \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

the equations (4) and (5) give the current function and velocity potential, and (7) and (8) the velocity components of a steady motion which, to the degree of accuracy indicated by (15), satisfies the condition that its surface, which is given by (11), may be a free surface.

Thus to this degree of approximation the form of the solitary wave is determined by (11), and we see that, since by (17) ma is essentially positive, the wave consists solely of an elevation, and that there cannot be a wave of depression capable of propagating itself unchanged with constant velocity: a result in accordance with the observations of Scott Russell.

We proceed to consider in greater detail the character of the approximation we have adopted for the free surface.

3. *The Surface Pressure in the Approximate Theory.*

The pressure at any point of a liquid in steady irrotational motion is given by the equation

$$p = \text{constant} - \tfrac{1}{2}\rho q^2 - gz, \quad . \quad . \quad . \quad . \quad (19)$$

where p and ρ are the pressure and density respectively. Over the free surface p ought to be constant: hence if δp denote the excess of pressure at any point of the surface given by (11) over the pressure at the mean level h in the motion just investigated, we have by (15) and (19)

$$\delta p = -4m^3\eta^2(\eta_0-\eta)\rho U^2 \cot mh \operatorname{cosec}^2 mh,$$

or

$$\delta p = -4g\rho m^2\eta^2(\eta_0-\eta)\operatorname{cosec}^2 mh. \quad . \quad . \quad . \quad . \quad (20)$$

Thus there is a defect of pressure everywhere but at the crest and the mean level. Note, however, how this negative pressure is distributed:—At the crest δp vanishes, and as it contains the factor $\eta_0-\eta$ and the crest is the point of *maximum* elevation, it remains very small over a long range on either side of the crest. Again, δp vanishes at mean level and remains very small over an infinite range. Finally, δp is a maximum at the point where $\eta=\frac{2}{3}\eta_0$, having then the value $-\frac{16}{27}g\rho m^2\eta_0^3 \operatorname{cosec}^2 mh$ (only $\frac{4}{27}$ of what the maximum would have been had we taken $3ma=2\sin^2 mh$): but this is at the point of inflexion (accurately when η_0/h is very small) where η is increasing most rapidly, and therefore this maximum pressure occurs where it can have least range. Thus we see that the pressure-error, small at its greatest, is so distributed as to be least effective.

4. *The Approximations of* Boussinesq *and* Lord Rayleigh.

We have found that to a high degree of approximation

the form of the solitary wave is given by the equations (11), (17), and (18), and its velocity of propagation by (16). We may from these eliminate, when required, any two of the three constants a, η_0, and m, but it is in general convenient to retain them, as each has a direct physical significance.

For purposes of approximation it should be noticed that when mh is regarded as a small quantity of the first order, then, by (17) and (18), ma will be of the second, and $m\eta_0$ of the third order. We proceed to consider certain rough approximations.

If in (11) we neglect m^2h^2 in expanding the cosine, &c., it reduces by means of (18) to

$$\eta = \eta_0 \operatorname{sech}^2 \tfrac{1}{2} mx, \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

which is the approximation to the surface obtained by Boussinesq, and again by Lord Rayleigh.

Similarly (17) and (18) give for a first approximation

$$m\eta_0 = \tfrac{1}{3} m^3 h^3 \text{ or } m = \sqrt{(3\eta_0/h^3)}, \quad . \quad . \quad . \quad (22)$$

as found by Boussinesq : Rayleigh obtained

$$m = \sqrt{\{3\eta_0/h^2(h+\eta_0)\}},$$

which is a little nearer, for, proceeding to the next approximation, (17) and (18) give

$$m = \sqrt{\{3\eta_0/h^2(h+\tfrac{1}{2}\eta_0)\}}. \quad . \quad . \quad . \quad . \quad (23)$$

Treating (16) similarly we obtain

$$U^2 = gh(1+\tfrac{1}{3}m^2h^2)$$

or

$$U^2 = g(h+\eta_0). \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

the approximation obtained by Boussinesq and Rayleigh, and the result originally deduced experimentally by Scott Russell and confirmed by Bazin *. It is, however, to be noticed that the experiments of Russell and Bazin cannot be regarded as capable of discriminating between the approximation of (24) and the more exact result given by (16). This will be sufficiently obvious to those who have had experience of such measurements, and it need only be pointed out that the experiments on which Russell relied to establish (24) were made in a long trough 20 or 30 feet long, and that, so far as I am aware, no allowance was made, nor I think could well have been made, for the influence of the successive reflexions from the ends.

* *Mém. des Savants étrangers*, tom. xix.

5. *The Wave-length.*

The solitary wave cannot directly be regarded as having any finite length as the elevation approaches the mean level asymptotically towards $x=+\infty$ and $-\infty$. Practically, however, Scott Russell found its length to be sufficiently definite to admit of his giving measurements of it. To obtain a measure Rayleigh suggested that the wave might be considered to end where its elevation became some definite and fairly small fraction, say 1/10, of its maximum elevation. Comparing, however, the formula (16) for the velocity with that in the ordinary theory of a train of waves, or the corresponding formulæ for ϕ, ψ, &c., it is natural to take for the wave-length $\lambda=2\pi/m$. If for an approximation we take the value of m given by (23), this gives

$$\lambda=2\pi\sqrt{\{h^2(h+\tfrac{1}{2}\eta_0)/3\eta_0\}}\;; \quad . \quad . \quad . \quad (25)$$

or, for waves just on the point of breaking,

$$\lambda=2\pi/m\doteqdot 2\pi h, \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

for in this case, as we shall see later, $mh\doteqdot 1$.

Curiously enough the formula (26) is that taken by Russell to represent approximately his experimental results, and it agrees well with (25), for all fairly high waves, such in fact as would be best suited for measurement. He noticed further that low waves were longer than high ones, which is also in accordance with (25); and thus altogether his results may be taken as giving a practical basis for the definition we have chosen, in addition to the theoretical one on which it is founded.

It should be noted, further, that this definition is practically of the kind suggested by Rayleigh, for, taking for the moment (21) as an approximation to the free surface, we see that taking $\lambda=2\pi/m$ is equivalent to regarding the wave as ending where $\eta/\eta_0=\operatorname{sech}^2\pi/2\doteqdot 0{\cdot}16$, or where the elevation is a little less than one sixth of the maximum.

6. *The Volume and Displacement of the Wave.*

The wave surface is given by (11), or, expanding by Lagrange's theorem, by

$$\eta=\frac{a\sin mh}{\cos mh+\cosh mx}+\frac{a^2}{2}\frac{d}{dh}\frac{\sin^2 mh}{(\cos mh+\cosh mx)^2}+\&c., \quad (27)$$

and the volume of the wave elevation per unit breadth of channel is

$$v=\int_{-\infty}^{\infty}\eta dx=2\int_{0}^{\infty}\eta dx. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

To perform the integration it is convenient to use the transformation

$$\int_0^\infty \frac{\sin^n mh\, dx}{(\cos mh+\cosh mx)^n}=\int_0^h \frac{(\cos m\theta-\cos mh)^{n-1}d\theta}{m\sin^{n-1}mh}=\mathrm{A}_n \text{ say.} \quad (29)$$

This gives, neglecting m^4h^5,

$$\mathrm{A}_1=h,\ \mathrm{A}_2\doteqdot\tfrac{1}{3}mh^2-\tfrac{1}{45}m^3h^4,\ \mathrm{A}_3\doteqdot\tfrac{2}{15}m^2h^3, \quad . \quad . \quad (30)$$

hence

$$v\doteqdot 2ah(1+\tfrac{1}{3}ma+\tfrac{1}{15}m^2a^2) \quad . \quad . \quad . \quad . \quad (31)$$

or, for a rough approximation, $v=2ah$.

Again, we see from (7) that the horizontal velocity in the wave-motion of all particles in the same vertical line is approximately the same, and that therefore each will be displaced through nearly the same distance as the wave passes over it. The average displacement δ of the particles is easily obtained, for as the wave passes completely across any section of the channel it must convey over it a quantity of liquid equal to its own volume, and this being done by the displacement of the particles we must have $v=h\delta$, or

$$\delta=v/h\doteqdot 2a(1+\tfrac{1}{3}ma+\tfrac{1}{15}m^2a^2). \quad . \quad . \quad . \quad (32)$$

The displacement of the particles comes, however, most naturally from the general discussion of the motion of the particles, to which we proceed.

7. *The Motion of the Particles.*

So far it has been sufficient to consider the steady motion resulting from the wave-motion by impressing on it a velocity equal and opposite to that of the wave propagation, but it now becomes necessary to consider the wave-motion itself.

Let ξ and ζ be the displacements parallel to the axes of x and z respectively at time t, of the particle which was initially, *i. e.* when $t=-\infty$, at x, z. Let ψ' and ϕ' be the current function and velocity potential respectively, at the point $x+\xi$, $z+\zeta$ at time t, and for brevity put $z'\equiv z+\zeta$, $x'=x+\xi-\mathrm{U}t$, then by (4) and (5)

$$\psi'=\mathrm{U}a\frac{\sin mz'}{\cos mz'+\cosh mx'}, \quad . \quad . \quad . \quad (33)$$

$$\phi'=\mathrm{U}a\frac{\sinh mx'}{\cos mz'+\cosh mx'}, \quad . \quad . \quad . \quad (34)$$

and from (7) and (8), or directly from (33) or (34), the components $\dot{\xi}$ and $\dot{\zeta}$ of the velocity $\dot{\sigma}$ will be given by

$$\dot{\xi} = \mathrm{U}ma \frac{1 + \cos mz' \cosh mx'}{(\cos mz' + \cosh mx')^2}, \quad . \quad . \quad . \quad (35)$$

$$\dot{\zeta} = \mathrm{U}ma \frac{\sin mz' \sinh mx'}{(\cos mz' + \cosh mx')^2}, \quad . \quad . \quad . \quad (36)$$

and

$$\therefore \ \dot{\sigma} = \mathrm{U}ma/(\cos mz' + \cosh mx'). \quad . \quad . \quad . \quad (37)$$

From (37) and (35) we see that the whole velocity and its horizontal component at any instant are nearly constant for all particles in the same vertical line, while the vertical component is, by (36), roughly proportional to the distance from the bottom. Further, from (37) we see that at the end of the wave, as we have defined it in Section 5, the velocity is only about 0·16 of the velocity in the centre of the wave, and that it decreases with extreme rapidity as we go further from the centre.

If θ be the inclination to the axis of x of the path of a particle initially at the distance z from the bottom, then by (35) and (36)

$$\tan\theta = \dot{\zeta}/\dot{\xi} = \frac{\sin mz' \sinh mx'}{1 + \cos mz' \cosh mx'}; \quad . \quad . \quad (38)$$

therefore, since initially $x' = \infty$, each particle begins to move forward from rest at an inclination, $\theta = mz$, proportional to its distance from the bottom and inversely proportional to the length of the wave ; its velocity goes on increasing till $x + \xi = \mathrm{U}t$, when it moves horizontally with its maximum velocity, and it finally returns to rest at an inclination $\theta = -mz$ equal and opposite to that with which it started. We proceed, however, to seek the actual paths described by the particles.

8. *The Paths of the Particles.*

If we integrate (36) we get

$$\zeta = \frac{a \sin mz'}{\cos mz' + \cosh mx'}. \quad . \quad . \quad . \quad . \quad . \quad (39)$$

This immediate integration depends on a peculiarity of fluid motions derived from steady motion by the addition of a motion of translation, which I have not seen noticed. In such motions the displacement, say ζ, perpendicular to the

impressed velocity, say $-U$, may be directly obtained from the current function, say ψ'. For

$$\dot{\zeta} = -\frac{d\psi'}{d\xi} = \frac{1}{U}\frac{d\psi'}{dt} = \frac{1}{U}\frac{\partial\psi'}{\partial t} = \dot{\psi}'/U.$$

$$\therefore \quad \zeta = \psi'/U,$$

d/dt being used to denote partial, and $\partial/\partial t$ complete differentiation with respect to t.

From (39) we see that a particle starting from the level z returns to the same level after attaining a maximum elevation ζ_0 given by

$$\zeta_0 = a \tan \tfrac{1}{2} m(z + \zeta_0). \quad . \quad . \quad . \quad . \quad . \quad (40)$$

which includes the special case of a surface particle given by (18).

To obtain ξ it is necessary to proceed by successive approximations. We find at once

$$\xi = a - a\frac{\sinh mx'}{\cos mz' + \cosh mx'} + \tau, \quad . \quad . \quad . \quad (41)$$

where the a is added to make the first part vanish when $x' = \infty$, or $t = -\infty$, and τ, which is of the order ma^2, is given by

$$\frac{\partial\tau}{\partial t} = \frac{\dot{\sigma}^2}{U} = \frac{Um^2a^2}{(\cos mz' + \cosh mx')^2}. \quad . \quad . \quad . \quad (42)$$

If we integrate this, using the transformation of which (29) is a case with special limits, and for brevity take advantage of the expressions (36) and (37), we get

$$\tau = ma^2\left\{\frac{\sin mz - mz\cos mz}{\sin^3 mz} - \frac{\dot{\xi}'/\dot{\sigma} - \sin^{-1}\dot{\xi}'/\dot{\sigma}.\cos mz'}{\sin^3 mz'}\right\} + \tau_1, \quad (43)$$

where again the first term is added to make the first part vanish when $x' = \infty$, and τ_1, which is of the order m^2a^3, may be similarly approximated to when wanted.

If we neglect τ, we find from (41) and (43) for the total displacement δ of any particle

$$\delta = 2a\left\{1 + ma\frac{\sin mz - mz\cos mz}{\sin^3 mz}\right\},$$

or, neglecting terms of the order $m^3a^2z^2$,

$$\delta = 2a\{1 + \tfrac{1}{3}ma\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

which shows that to this order all particles are equally displaced by the wave. The agreement of (44) with (32), which is obtained very differently, may be noted in passing.

The path of any particle is given by (39), (41), and (43), but if we neglect τ, we can at once eliminate x' from (39) an (41), and obtain

$$(\xi-a)^2+\zeta^2+2a\zeta\cot m(z+\zeta)=a^2. \quad . \quad . \quad (45)$$

If we expand this, neglecting ζ^2 as it is of the same order as a^3, we get

$$(\xi-a)^2+2a\zeta\cot mz=a^2 \quad . \quad . \quad . \quad . \quad (46)$$

as an approximate equation to the path described by any particle originally in the plane z. To this order, therefore, each particle initially at a distance z from the bottom describes that part of the parabola given by (46) which lies above the level z. This gives $2a$ for the maximum horizontal displacement, and $\frac{1}{2}\,a\tan mz$ for the maximum elevation, of a particle, but more exact values have already been given in (44) and (40).

9. *The Energy of the Wave.*

The potential energy of the wave per unit breadth is

$$V=\tfrac{1}{2}g\rho\int_{-\infty}^{\infty}\eta^2dx=g\rho\int_0^{\infty}\eta^2\,dx:$$

but, by Lagrange's Theorem, (11) gives

$$\tfrac{1}{2}\eta^2=\frac{a^2}{2}\frac{\sin^2 mh}{(\cos mh+\cosh mx)^2}+\frac{2a^3}{3}\frac{d}{dh}\frac{\sin^3 mh}{(\cos mh+\cosh mx)^3}+\&c.$$

Hence by (29) and (30),

$$V\doteqdot\tfrac{1}{32}g\rho ma^2h^2(1+\tfrac{7}{10}ma). \quad . \quad . \quad . \quad . \quad . \quad (47)$$

The kinetic energy per unit breadth is

$$T=\iint\tfrac{1}{2}\rho\sigma^2dx\,dz,$$

the integration extending throughout the liquid.
Thus

$$\begin{aligned}T&=\tfrac{1}{2}\rho\iint\{(U+u)^2+w^2\}dx\,dz,\\&=\tfrac{1}{2}\rho\iint U^2dx\,dz+\rho\iint Uu\,dx\,dz+\tfrac{1}{2}\rho\iint q^2dx\,dz,\\&=\tfrac{1}{2}\rho U^2\iint dx\,dz+\rho U\iint d\psi\,dx+\tfrac{1}{2}\rho\iint d\phi\,d\psi.\end{aligned}$$

$\therefore$ by (4) and (5),

$$T=\tfrac{1}{2}\rho U^2(c-2ah): \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

or, using the approximation (31),

$$T\doteqdot\tfrac{1}{32}\rho U^2\,ma^2h(1+\tfrac{1}{5}ma).$$

Hence, substituting for U, we have to the same order

$$T \doteqdot \tfrac{1}{3} g\rho m a^2 h^2 (1 + \tfrac{7}{10} ma) ; \quad . \quad . \quad . \quad . \quad . \quad (49)$$

so that the kinetic and potential energies are equal to this order of approximation at least.

10. *The Limiting Height of the Wave.*

It is found by experiment that there is a limit to the height of the solitary wave depending on the mean depth of the liquid : when an attempt is made to form a higher wave, it breaks at the crest.

Since q^2 cannot be negative, the limiting form will be that for which $q=0$ at the crest, and therefore by (14) and (16), the greatest elevation of crest will be given by

$$2m\eta_0 = \tan mh. \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

Now by (6) we see that when $u=0$ at the crest

$$ma = 2\cos^2 \tfrac{1}{2} m(h+\eta_0),$$

and therefore by (18)

$$m\eta_0 = \sin m(h+\eta_0). \quad . \quad . \quad . \quad . \quad . \quad (51)$$

Solving (51) and (52) for mh and $m\eta_0$ we find

$$mh \doteqdot 1{\cdot}1, \quad m\eta_0 \doteqdot {\cdot}9 \quad . \quad . \quad . \quad . \quad . \quad (52)$$

so that the wave will break for an elevation rather less than the mean depth. It is needless to seek to specify the breaking elevation more exactly, for the approximation is here pushed to an extreme limit. In fact, by (4), the crest when $q=0$ becomes a double point on $\psi = -Uh$, and the branches cut at right angles, whereas Stokes has shown that for a free surface the crest angle must be $2\pi/3$ at the breaking-point. Our approximation, however, considering the extreme circumstances, is sufficiently fair to indicate that the conditions (52) for breaking should not be far wrong. Scott Russell's experiments confirm this : he found that the wave broke when the elevation was about equal to the depth ; but from some experiments of my own I am inclined to think that $\eta_0 = 3/4h$ is a closer approximation for the elevation at the breaking-point.

11. *Approximate Theory of Breakers.*

Some account can be given of the gradual increase in height and ultimate breaking of waves rolling in on a gently sloping beach.

We have seen that to a first approximation the volume of the wave per unit breadth of channel is $2ah$, and to the same order we easily obtain also

$$v = 2\,ah = \frac{2}{\pi}\lambda\eta_0 = 4\sqrt{\eta_0 h^3/3} \quad , \quad . \quad . \quad . \quad (53)$$

the approximations being fair for low waves.

Now as the wave rolls in its volume remains constant, and therefore its height increases and length diminishes as the depth diminishes, or exactly

$$\eta_0 = \frac{3}{16}\frac{v^2}{h^3}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

so that the elevation varies inversely and the length directly as the cube of the depth. As the wave becomes higher it will be necessary to take the more exact formulæ instead of (53). By (52) when the wave is on the point of breaking $mh \doteqdot 1$ and $ma \doteqdot 2/3$, and so using the more exact formula (31) for the volume we get roughly

$$v = 1{\cdot}5h^2 \text{ or } h = {\cdot}8\sqrt{v},$$

which gives the depth in which the wave will break.

Thus the big waves will break first, and the depth in which they break will vary as the square root of their volume.

12. *The Views of* Sir George Stokes—*Conclusion.*

Having thus examined in some detail the approximation to the solitary wave which is obtained by taking the first term only of (2), and having seen that even this first approximation satisfies to a high degree of accuracy the condition for the propagation of the wave without change, we are naturally led to examine the argument given by Stokes, in his paper "On the Theory of Oscillatory Waves," already cited, against the possibility of the propagation without change of form or velocity of any other form of wave than the infinite train of "oscillatory" waves which he there discusses—to a degree of approximation not quite so close as that with which we have been occupied in the foregoing sections.

Having found (§ 4) for the velocity of propagation U of any wave form in liquid of depth h,

$$\mathrm{U}^2 = gm^{-1}\tanh mh,$$

and having previously (§ 2) put aside "imaginary" values of the m as inadmissible, he infers that, since this will give only one value ($\pm$) of m for a given value of U, there can

only be one form for each velocity. In the light of equation (16) above, the oversight in discarding the "imaginary" value is obvious. It is too hastily concluded that such a value would imply infinite velocity &c. either when $x=+\infty$ or when $x=-\infty$, but this is not necessarily so, though it is too frequently assumed in such like investigations, for in fact the value of ϕ given in (5) above gives a well-known expansion of the form $\Sigma A\epsilon^{ax+bz}$ such as is considered by Stokes, but the "real" coefficients p are *discontinuous, changing sign with* x, so that ϵ^{pr} vanishes both for $x=+\infty$, and for $x=-\infty$.

We may conclude, then, that we have obtained just as satisfactory evidence for the unchanging propagation of the solitary wave as there is for that of the infinite train investigated by Stokes. In a Supplement to his paper published in 1880*, he has carried his approximation one step further, and we may with advantage employ a somewhat similar method in proceeding to higher degrees of approximation for the solitary wave. Proceeding on the same principles by which we obtained (1) and (2), we may take instead

$$U(z+\iota x)=-(\psi+\iota\phi)+\Sigma A_{2i+1}\tan^{2i+1}\tfrac{1}{2}m(\psi+\iota\phi)/U\ . \quad (55)$$

which leads to the higher approximations with considerably less labour, though to the order with which we have been occupied it offers no advantage, in fact rather the reverse from its indirect character.

VIII. *Acoustic Thermometer—a Suggestion.* *By* S. Tolver Preston†.

THE following may have more theoretical than practical interest (illustrative of a connexion between acoustics and heat); but perhaps ingenuity might give the suggestion also a practical value. The idea is simple enough, and relates to the varying note afforded by a resonance-tube according to the temperature of the enclosed air or gas; the notion being to employ this in some way as a measure of temperature. I shall only illustrate, however, the simplest aspect of the case.

Thus, for mere theoretical illustration, we may suppose a tube, closed at its inner end, to be inserted somewhere in the wall of some furnace, or buried in some less heated object, whose temperature is to be estimated. Of course a tuning-fork of a certain vibrating period will, at normal temperature,

* Collected Papers, vol. i.

† Communicated by the Author.

vibrate in resonance with the tube possessing a certain length. Then it will be seen at once that changing the temperature of the object where the tube is placed will alter this state of affairs. Another fork of different vibrating period must now be selected in order to resound with the tube. Of course there are certain relations between the vibrating period and the temperature, and it is to illustrate the extreme simplicity of these relations under the kinetic theory of gases that is one point in the present paper.

Maxwell showed, in his celebrated paper, "On the Dynamical Evidence of the Molecular Constitution of Bodies," published in 'Nature,' March 4, 1875, that it was demonstrable *mathematically* that "the pressure of a gas cannot be explained by assuming repulsive forces between the particles. It must therefore depend, in whole or in part, on the motion of the particles" (Maxwell's paper, p. 358).

Hence it appears so far clear, as we may say, that we must have recourse to a dynamical theory in order to explain one of the simplest and most fundamental properties of a gas.

A confidence in the dynamical theory led me (Phil. Mag. June 1877) to suggest its application to illustrate the mechanism of the propagation of sound in gases; and the very simple relation showed itself, viz. that the velocity of propagation of sound could only depend on the velocity (normal) of the molecules of gas themselves, and on nothing else; in fact, that the sound-wave moved independently of the density and pressure of the gas. Indeed, according to the kinetic theory, the molecules of the gas have of course no distant action on each other, and can therefore only influence each other by impact (so that the velocity of the normal motion of the molecules of the gas alone comes into play in propagating the wave).

Now this applies very simply, as will be apparent at once, to our proposed acoustic thermometer. For it is this normal motion of the molecules of the gas (in the tube), the energy of which motion we call the "temperature," which is the sole factor in determining the velocity of sound, of which the tuning-fork (we employ with the tube) is the mechanical indicator. The velocity of sound being as the velocity of the gaseous molecules, and velocity of the molecules being as the square root of their energy, then, since the temperature *is* the energy, the velocity of sound in a gas is proportional to the square root of the temperature, as we see.

If we have a tuning-fork whose vibrating period is mechanically adjustable, it is easy to perceive, then, from the above, that the temperature (in the tube) is inversely propor-

tional to the square of the vibrating period of the fork; or, if the length of the tube be adjustable, *i. e.* if the tube be telescopic, the temperature of the air in the tube (therefore of the heated receptacle or what not, in which the tube is placed) is evidently proportional to the square of the length of the adjustable tube.

Zero Centigrade being 273 above the absolute zero, the Centigrade zero is then, of course, 273 when expressed as absolute temperature. At 273 above zero C. (which is 546 of absolute temperature) the molecules of air have, of course, twice the energy they have at zero C. At 4×273 absolute temperature (819 above zero C.) the molecules of air will possess, in the same way, four times the energy possessed by them at zero C., and therefore twice the velocity which they had at zero C. (velocity being as the square root of energy). Sound would then be propagated in air (in such a tube) whose temperature is 819° C. at twice the velocity of its transmission in air at 0° C. So that a tube of air at a temperature of 819° C. would be in resonance with the same tuning-fork as a tube of half the length resounds to at 0° C. This is sufficiently clear; and so it is evident that varying the length of a telescopic tube and employing a constant fork serves the same object as (conversely) varying the vibrating period of an (adjustable) fork and keeping the length of the tube constant. Some may see a way to propose some modification of the above, in a mechanical point of view, which might be more sensitive. It is the principle, or rather the theoretical aspect of the case, with which we are chiefly concerned.

Hamburg, May 1, 1891.

IX. *On a Modified Form of Wheatstone's Bridge.* *By* R. A. Lehfeldt, *B.A., B.Sc., Demonstrator at Firth College, Sheffield**.

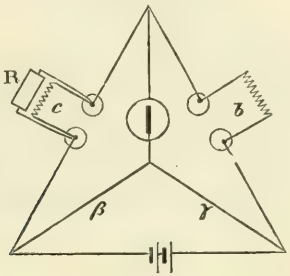
In comparing the resistances of two nearly equal coils, a fine adjustment may be obtained either by a divided wire of low resistance in series with the coils, or by a resistance-box in parallel with them. The latter method, involving only a piece of apparatus that exists in every laboratory, appears to be somewhat simpler than the more common one, for which a specially mounted wire is required; and it avoids,

* Communicated by the Author.

moreover, the disadvantage of a sliding contact. It may, therefore, be worth while to give some details of its use.

In Wheatstone's Bridge, let β and γ (fig. 1) be nearly equal resistances permanently mounted. Let b and c be the

Fig. 1.



coils to be compared, R a resistance-box in parallel with the higher of the two. Let b_1, c_1 be the resistances of the connexions of b and c. Put

$$\frac{c\mathrm{R}'}{c+\mathrm{R}'}=c';$$

then

$$(c'+c_1)\gamma=(b+b_1)\beta.$$

If c and R be interchanged with b and R has to be altered to R′ for balance, putting

$$\frac{c\mathrm{R}'}{c+\mathrm{R}'}=c'',$$

then

$$(c''+b_1)\beta=(b+c_1)\gamma.$$

Hence

$$b=\tfrac{1}{2}\left(\frac{c'\gamma}{\beta}+\frac{c''\beta}{\gamma}\right)+\frac{(b_1\beta-c_1\gamma)(\beta-\gamma)}{2\beta\gamma}.$$

The second term, on the right-hand side, is of the second order of small quantities; and as β and γ should be within $\frac{1}{1000}$ of one another, while the resistance of the copper strip and mercury-cup connexions is very small, it may be neglected. Therefore,

$$b=\tfrac{1}{2}\left(\frac{c'\gamma}{\beta}+\frac{c''\beta}{\gamma}\right);$$

put $\gamma=\beta(1+\delta)$, where δ is small. Hence

$$b=c'(1+\delta)+c''(1-\delta)=\frac{c'+c''}{2}+\frac{\delta}{2}(c'-c'').$$

Here, again, the second term on the right-hand side is of the second order, so we get simply

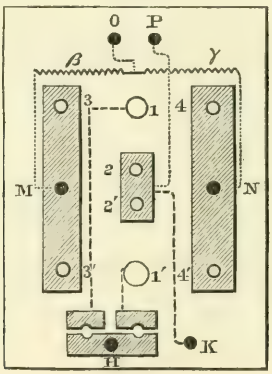
$$b = \frac{c' + c''}{2};$$

or, the resistance of b is the mean of the two values of c and its shunt obtained by reversing.

The switch-board used by S. P. Thompson in carrying out Carey Foster's method of comparing resistances may easily be adapted to the shunt method. But a switchboard designed for the purpose is more convenient: this form may be suggested.

In fig. 2 the shaded parts represent solid brass or copper pieces:

Fig. 2.



the dark circles binding screws, the light ones mercury-cups. The coils to be compared are put between 1 and 2 and 1′ and 2′. The terminals of the resistance-box are connected to H, K, so that by inserting a plug it can be put in parallel with either of the coils.

1 and 1′ are then connected by copper bars either to 3 and 4′ or to 4 and 3′. The equal resistances β and γ are of course wound on the same reel, and may be soldered permanently in place. M, N are the battery terminals, O, P those of the galvanometer.

If the coils to be compared differ as much as a B.A. unit does from a legal ohm, the resistances taken from the box will give the difference to ·0002 ohm, and interpolation by means of the galvanometer deflexions need only be resorted to beyond that. The sensitiveness of the method is of course limited by that of the galvanometer.

Appendix.

From the original equations,

$$c' = \frac{b\beta + b_1\beta - c_1\gamma}{\gamma},$$

$$c'' = \frac{b\gamma + c_1\gamma - b_1\beta}{\beta}.$$

Hence with $\gamma = \beta(1+\delta)$ it follows

$$c' - c'' = -2b\delta + 2(b_1 - c_1) - \delta(b_1 + c_1);$$

the third term on the right-hand side is of the second order of small quantities ; and in any symmetrical switchboard the second term will be exceedingly small, so we have nearly

$$\delta = \frac{c'' - c'}{2b}.$$

The ratio δ of the nearly equal arms β and γ can thus be readily tested.

X. *A Steam-Engine Indicator for High Speeds.*

By Prof. John Perry, *F.R.S.**

MEMBERS who are not practically acquainted with the errors of the ordinary steam- or gas-engine indicator are referred to a paper in the 'Proceedings of the Institution of Civil Engineers' (vol. lxxxiii. 1885) by Professor Osborne Reynolds, and an exhaustive discussion of the subject.

Whether we do or do not share Prof. Reynolds's view that even at low speeds of engines the errors in calculating horse-power are very considerable, because of the friction of the paper barrel and the stretching of the cord or wire which gives to the paper barrel a miniature motion of the engine piston, it is obvious that there will be more confidence in an indicator in which the motion-copying mechanism gives a very short stroke, is opposed by very small forces, and requires no string or wire. I do not pretend to get rid of the error in a spring which is due to change of temperature, but where great accuracy is required it is always worth while, when using this or any other indicator, to have a "boiler-pressure" line drawn upon the diagram, as well as an "atmospheric line;" and these two lines, with a pressure-gauge on the boiler, will give the scale to which the indicator at the time

* Communicated by the Physical Society : read May 22, 1891.

represents pressure and prevent error due to change of temperature of the spring.

In these days of high-speed machinery the most important defect of an indicator is its slow natural period of vibration. If the natural period of vibration is from $\frac{1}{20}$ to $\frac{1}{30}$ of the time of revolution of an engine, it is found that the diagram is not deformed by waviness, ordinary fluid friction destroying the natural vibration; if it is as much as $\frac{1}{15}$, a considerable amount of pencil pressure must be employed to obtain a frictional stilling of vibration; but if it is as low as $\frac{1}{10}$ it is almost impossible, even with great pencil friction, to obtain a decent diagram. To make an indicator have a quicker natural vibration it is necessary to use a stiffer spring, and this means that pressures are indicated to a very small scale. Introducing seven per cent. of inaccuracy in area of diagram, either by friction or smallness of scale, may possibly allow the very best existing indicator to be used on engines of as high a speed as 400 revolutions per minute; but this is a matter on which assertions are made of higher and very much lower limits of speed than what I have stated. I think that users of indicators will generally agree that I have not exaggerated this defect; but unfortunately there is scarcely ever any kind of check which can be applied to a measurement of indicated horse-power, so that mere assertions are of very little value.

Indicated horse-power is now the sole standard of the values of engines, so that its accurate measurement is very important; but for the inventor and improver of engines, and for the physicist, that there shall be no local deformations in the shape of the indicator-diagram is of greater importance than that its area should be correct. Now the natural period of vibration of the indicator before you is about $\frac{1}{500}$ of a second; allowing twenty periods to one revolution of the engine, I find that this indicator will give diagrams with no wave-deformations until the speed of the engine exceeds 1500 revolutions per minute. I can, however, by changing the disk make the natural period of vibration $\frac{1}{1000}$ or $\frac{1}{250}$ of a second, or, indeed, what I please, so that there is practically no speed at which this indicator will not give a true diagram.

Specimens of the indicator are before you, but I will throw upon the screen drawings of it. Fig. 1 is a section, and fig. 2 an elevation. It consists of a very shallow circular box, E, of metal (in some of my specimens it is of cast iron, in others of gun-metal) closed by a thin disk of steel, D. Here, for example, is one an inch and a quarter in diameter, and about $\frac{1}{60}$ of an inch thick, which I use for

maximum steam-pressures of about 30 lb. to the square inch above the atmosphere. It was my intention to use corrugated disks, but as these could not be obtained cheaply, except in quantity, I have hitherto used plane disks, and found them quite satisfactory for such sizes of diagram as I have hitherto dealt with. I am, however, making arrangements for obtaining corrugated disks for use in the indicator.

Fig. 1.

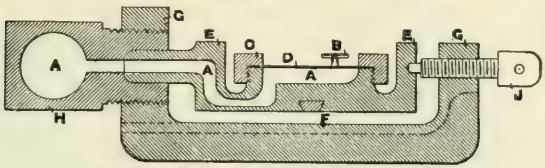
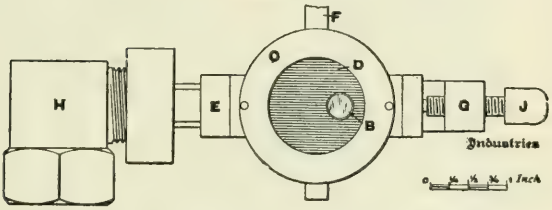


Fig. 2.



Now when this box E is put in communication with the cylinder of a steam-engine in the usual way, that is through the pipe A and the indicator-cock, the disk yields more or less as the pressure is greater or less. To magnify this yielding I fix upon the disk, about halfway between its centre and circumference, a small mirror B such as is used in electrical laboratories. This mirror has a light frame of metal, and can be screwed to or unscrewed from any of these disks quite readily. I let a beam of light from an ordinary oil-lamp fall upon the mirror, and it is reflected and falls upon a sheet of white paper which it illuminates at a small spot. Now the yielding of the disk under fluid pressure is evidenced by the movement of the spot of light on the paper. For example, if steam of 10, 20, or 30 lb. pressure per square inch (above the atmosphere) is admitted to this box with its present disk, and the spot of light is on a sheet of paper about 4 feet away from the mirror, the spot will be seen to travel one, two, or three inches from its original position. If there is a partial vacuum inside the box, the spot travels in the opposite direction. It will be seen, therefore, that I have

used a reflected beam of light as if it were a rigid pointer four feet long. By using a lens, by using magnesium light instead of a common oil-lamp, and by taking certain precautions which are quite obvious to the members of this Society, I could throw a well-defined spot upon a screen forty feet away from a mirror upon a small corrugated disk, whose motion would be with great exactness proportional to the pressure, for motions of as much as five or six feet.

The end of the arm F receives a miniature motion of the piston of the engine by stiff rods, and this causes the spot to move at right angles to its former motion; and when both motions are being given the spot travels round on the screen, its position at any instant indicating the pressure of the steam and the position of the piston in its stroke.

Now, although I have never heard of such a method being used, I feel that many people must have thought of using it. I myself thought of it many years ago; but the making of a photographic record seemed to me to introduce great difficulty, so I never tried it*. What I have now discovered is this, that a photographic method of recording is quite unnecessary. In fact, even at speeds of 60 revolutions per minute the image of the spot remains on the retina sufficiently long to enable a man to draw upon the screen the path of the spot. He first turns the indicator-cock, so that there is atmospheric pressure under the disk. The spot now travels in a straight line, and this is the atmospheric line. When I wish to check the scale I do what I should like to see done with all indicators, I let steam at boiler-pressure underneath the disk and mark out another straight line parallel to the atmospheric line. I now let the box communicate with the cylinder, and I draw the actual diagram. A very little practice will enable anyone to draw the diagram quite accurately, even when the engine makes only 60 revolutions per minute. But at such speeds as 150 revolutions per minute, the diagram is quite continuous as a thin line of light on the paper, and the most unskilled person need not make errors of as much as one per cent. in drawing a pencil line, which remains quite visible in the middle of the thin line of illumination.

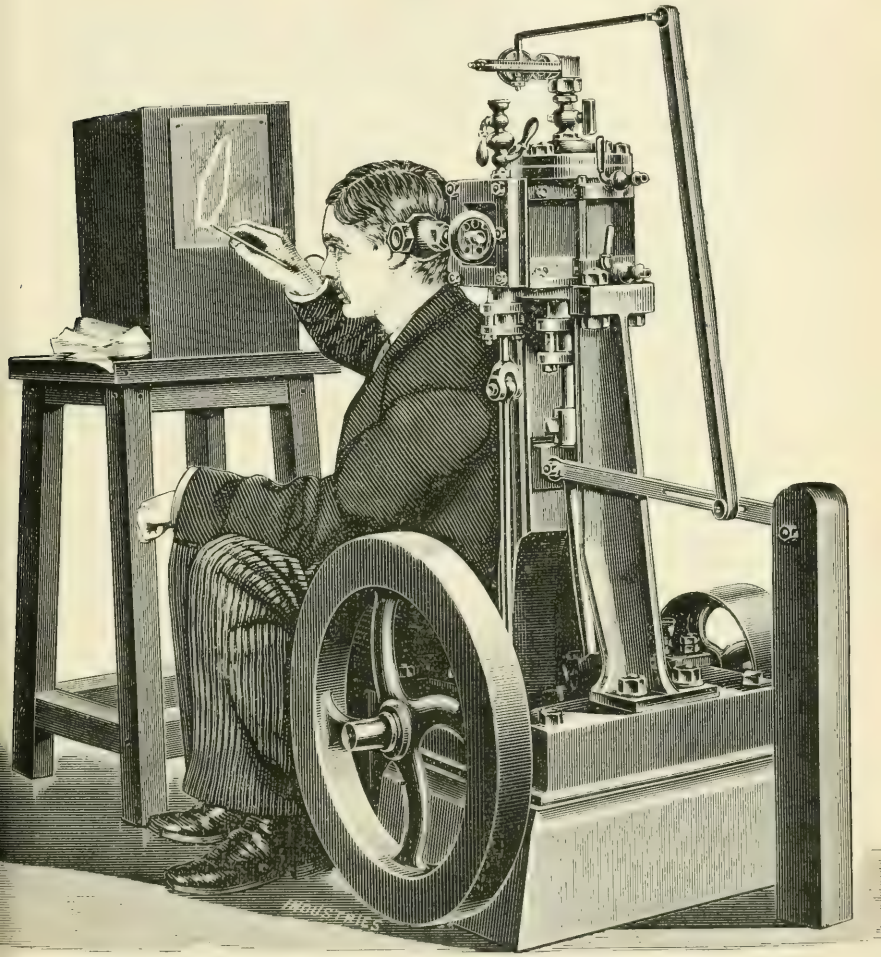
Using a common oil-lamp, a diagram about six inches long and four inches broad, formed of a band of light one tenth of an inch broad, is quite visible even in a well illuminated room. If the room is darkened the diagram becomes quite

* Prof. R. H. Smith has, since the reading of the paper, called my attention to an indicator described in 'Engineering' of July 10th, 1885, by Messrs. Clarke and Low, in which a reflected beam of light is used for magnification.

vivid, and to anyone accustomed to indicator-diagrams it is an object of interest from quite a number of considerations.

As I am unable to show to the Society this instrument in action, I will throw upon the screen a photograph, fig. 3,

Fig. 3.



taken at Finsbury of the indicator placed upon a toy steam-engine, which some of my students made to drive testing machines. My partner, Mr. Holland, is following the spot of light with a pencil. As a matter of fact, the engine was really at rest, and the diagram was drawn as a thick chalk

line upon dark paper, when this photograph was taken; but if an instantaneous photograph had been taken of the arrangement actually working, it would not have been very different from what I here show, except that the line of light forming the diagram would have been finer.

We have only been able to run this toy engine at a maximum speed of about 900 revolutions per minute, and indeed at this speed it was rather dangerous to run it, as, through want of balance, it set the floor and everything in the room a-shaking; but even at this high speed there was no evidence on the diagram of any waviness due to the natural vibrations of the disk of the indicator. There was, however, a musical note in evidence of the existence of such vibrations.

Mr. Holland has used a tapering wooden box as if it were a camera for photographing the diagram and its atmospheric line, and he tells me that it is quite easy to take such photographs. He is, however, accustomed to such work, and I do not think that an ordinary engine-driver would care to try the photographic method. I here exhibit some of Mr. Holland's photographs. This one, fig. 4, required an exposure of one minute, the light being that of an ordinary

Fig. 4.

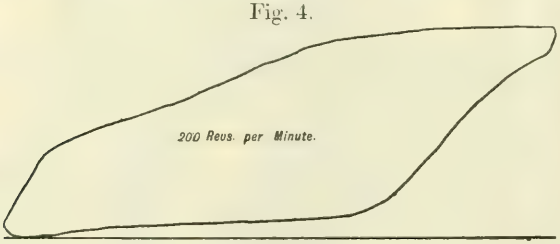
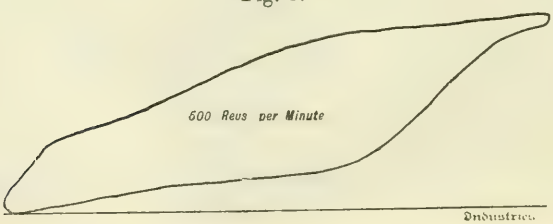


Fig. 5.



oil-lamp. This one, fig. 5, required an exposure of ten seconds, the light being obtained by the burning of a piece of magnesium strip behind the hole.

I have, however, used Mr. Holland's box with sheets of tracing-paper instead of photographic plates, and the indicator-

diagram is now an object which is very easily observed and traced.

I exhibit a few drawings made on tracing-paper in this way by Mr. Holland. First, we have a few taken at about the same time; these taught us that we had better make considerable changes in the valve of our engine. We made these changes, and here are some others taken subsequently. The speed and other necessary information are given on each sheet of paper, so that the effect of change of speed on our toy engine may be noted.

With an ordinary indicator the instrument must be stopped in its action, and a sheet of paper taken from the drum, before the diagram can be looked at. But here the diagram is visible all the time. To the student or improver of steam-engines it is very instructive to keep looking at the diagram whilst altering steam-pressure, or speed, or load of the engine, and it is an amusement of which one does not very soon become tired. Even with this toy engine of mine I have already observed such changes in the shape of the diagram as have thrown a perfectly new light upon the condensation phenomena occurring inside a steam-engine cylinder.

The first form of this new indicator is lying on the table. You will see that to give it the piston motion in miniature required considerable force to be exerted, a fault which I have corrected since. Now the very first time the instrument was tried a very curious phenomenon was observed, namely, that the indicator-diagram was not one continuous line of light, but a series of "blobs" or spots, connected by a much fainter line. I easily saw that these indicated a vibration going on in the rods which gave to the box the motion of the piston in miniature. I found that the cause of this was due to the bad fitting or "backlash" in a lever which my students had been in the habit of using with ordinary indicators on the same engine. With an ordinary indicator there was no possibility of observing from the diagram that such a fault existed, and was probably greatly accentuated by the use of a cord instead of our rod; here it was very evident. Indeed, although only to a small extent, it will be observed in the photographs that there are regular changes of intensity of light in every diagram, and that this vibration of the piston-motion mechanism has not been altogether done away with even in our more carefully fitted stiff rods.

Added, June 5th, 1891.

In the discussion which followed the reading of the paper

it was suggested by Mr. Swinburne that the most useful function of such an indicator would be to continually show the diagram on a screen in an engine-room, so that at every instant the engineer would not only know the pressure of steam in his boiler, but also the pressure at every instant in the cylinder.

I quite forgot to put this in my paper, although its importance was not unknown to me. I am now attaching an indicator to each end of the cylinder of my driving-engine at Finsbury. These will receive their miniature piston-motion from one rod. One gas-jet will throw from the two mirrors two diagrams upon a screen some seven feet away from the mirrors, and these diagrams will be visible from nearly every part of the engine-room at all times. In the room at present there are not only very visible pressure- and vacuum-gauges and a speed-indicator (not a counter), but also a dynamometer coupling, which shows at a glance the actual horse-power which is being transmitted along a shaft. If, instead of tracing the diagram with a pencil, I were to trace it with the point of a planimeter, the reading might represent the horse-power.

It is unnecessary to describe here how the indicator might be fixed to the valve-chest or receivers, or to other parts of an engine, such as the air- and force-pumps; or to pumping-machinery generally; or to engines driven by fluids. In fact it may be said that I have made the discovery that the beautiful method of observation of vibration of M. Lissajous has hitherto been neglected in its applicability to all sorts of practical purposes. Quite a number of other applications of the reflected beam of light principle suggest themselves.

PM 32 (1891)

XI. *On the Value of some Mercury Resistance Standards.* *By* R. T. Glazebrook, *M.A., F.R.S., Fellow of Trinity College, Cambridge* *.

IN a paper read before the Physical Society * on May 23, 1885, I described the results of a comparison between the original standards of the British Association and some copies of the mercury unit representing Legal Ohms made by M. Benoit in Paris and sent to me by him. Two of these copies have remained in my possession since that time; the third, at M. Benoit's request, was handed to Mr. Preece.

* Communicated by the Physical Society: read May 9, 1891.

† Glazebrook, Phil. Mag. October 1885; Proc. Physical Society, vol. vii.

The mercury with which the tubes were filled in 1885 has remained in them since that date. Now recent observations had seemed to indicate that a small change had taken place in some of the platinum-silver standards, and it became desirable to compare them again with M. Benoit's tubes. The method was the same as that of my former paper. The tubes immersed in melting ice were compared with the B.A. standards. The temperature of the room was kept very low, from 0°·5 to 3° C., and thus the errors caused by the conduction of heat into the tubes through the copper connecting rods were avoided. The connecting pieces used to connect the tubes to the bridge differed from those employed in 1885, being a modification of the platinum cups described in my paper * on the specific resistance of mercury. A hollow platinum cup, about 3·5 cm. long and rather more than 1 cm. in diameter, is secured firmly into an ebonite tube ; the outside of the tubes are turned to fit the ground portion of the glass vessels which form the ends of the mercury tubes, thus taking the place of the stoppers which usually close the tube ; the platinum cups dip into the mercury, the surface of contact being about 12 sq. cm. The cups had previously been platinized ; on the present occasion they were merely cleaned with nitric acid and distilled water. Stout copper rods, well amalgamated, fit tightly into the inside of the cups ; the other ends of these rods are in contact with the bridge. Thus the connexion with the bridge is made through the rods and across the platinum of the cups, avoiding contact between the mercury and copper.

The resistance of the connexions was determined, and it was shown that the resistance of the platinum was negligible. This was done by making the rod and cup part of a circuit, the resistance of which was measured. The rod was then removed from the cup, and the latter was removed, so that the part of the copper which had been in the cup was now in direct contact with the mercury into which previously the cup had dipped. No change in the resistance of the circuit was produced by this. To secure this result it was necessary that a considerable area of the platinum should dip into the mercury ; and this condition was in the experiments always carefully attended to. The resistance of these connecting-pieces was thus found to be ·00291 B.A. unit.

The tubes were compared both with the B.A. units and also with the Legal-Ohm standards. In the comparison with the B.A. units, a large amount—about 300 divisions, or ·015 B.A. unit—of the bridge-wire was used. Since the resistance of the

* Phil. Trans. 1888.

bridge-wire is known at 15°, this required, when the temperature of the room was as low as 1° or 2°, correcting for temperature; but as the whole correction amounted to less than 2 per cent. of the bridge-wire used, while this again was only 1·5 per cent. of the resistance measured, no very accurate knowledge of the temperature of the wire was needed. In some cases a coil of 100 B.A. units was put in multiple arc with the mercury tube; and the resistance of the combination, which amounted to a little over 1 B.A. unit, was compared with the wire standard.

The results of the comparisons are given in the following Tables.

Table I.—Tube, Benoit No. 37.

Date.	Standard.	Notes.	Value in B.A. units.
Jan. 3.....	Flat.	.....	1·01111
„ 5.....	Flat.	.....	1·01103
„ 5.....	Flat.	100 B.A. units in multiple arc with tube.	1·01108
„ 6.....	Flat.	.....	1·01099
„ 6.....	Flat.	Mercury drawn through.	1·01101
„ 7.....	Flat.	.....	1·01109
„ 7.....	Flat.	Mercury drawn through.	1·01109
„ 7.....	Flat.	After interval of 1 hour.	1·01106

Mean for No. 37..... 1·01106 B.A. units.

Table II.—Tube, Benoit No. 39.

Date.	Standard.	Notes.	Value in B.A. units.
Jan. 3.....	Flat.	.....	1·01053
„ 5.....	Flat.	.....	1·01058
„ 5.....	Flat.	100 B.A. units in multiple arc with tube.	1·01060
„ 6.....	Flat.	.....	1·01049
„ 6.....	Flat.	Mercury drawn through.	1·01037
„ 7.....	Flat.	.....	1·01041
„ 7.....	Flat.	Mercury drawn through.	1·01034
„ 7.....	Flat.	After interval of 1 hour.	1·01029
„ 8.....	Flat.	.....	1·01022
„ 8.....	Flat.	Mercury drawn through.	1·01027
„ 8.....	Flat.	After interval of 1 hour.	1·01033

Mean of last seven for No. 39..... 1·01032.

With regard to the observations on No. 37, it will be seen that they are extremely close, the greatest difference between

any two is ·00012 B.A. unit, or rather more than 1 in 10,000; and no appreciable change was produced by passing the mercury through the tubes. The observations on No. 39 are not quite so close. On January 6 a distinct change was caused by passing the mercury through; after that date the results are fairly consistent, and no further alteration was observed; the mean of the values found after this date may be taken as the resistance of the tube to an accuracy of about 1 in 10,000.

The two results therefore are:—

No. 37..... 1·01106 B.A. units.
No. 39..... 1·01032 B.A. units.

The observations in 1885 were reduced to Legal Ohms, using the value for the resistance of mercury in terms of the B.A. unit adopted by the B.A. Committee in that year, and based on Lord Rayleigh's experiments. According to this 1 Legal Ohm = 1·0112 B.A. units.

If we take these values we have as the resistances in Legal Ohms the following:—

	Benoit.	R. T. G. 1885.	R. T. G. 1891.
37	1·00045	·99990	·99986
39	·99954	·99917	·99913

Comparing the last two columns we see that the tubes have apparently fallen in value relative to the standard Flat in the $5\frac{1}{2}$ years by ·00004, but this quantity is too small to be really certain of. The results of the experiments therefore prove within this limit that the platinum-silver coil Flat has not altered relative to the mercury-tubes in this interval. The difference between the values found by Benoit and myself depends on the value used for the resistance of mercury in B.A. units. According to Lord Rayleigh *, the resistance of a column of mercury 100 cm. long, 1 sq. mm. in section, at 0° C., is ·95412 B.A. unit, and this is the value which has been used in the above. The value found by Mr. Fitzpatrick † and myself for this resistance was ·95352. Practically the same number has been obtained by Wuilleumeier ‡, Hutchinson §, and Salvioni ‖. If this number be adopted, then

1 Legal Ohm = 106 × ·95352 B.A. unit.
= 1·01073 B.A. units.

* Phil. Trans. 1883.
† Phil. Trans. A. 1888.
‡ Wuilleumeier, *Comptes Rendus*, cvi., 1888.
§ Hutchinson, Johns Hopkins University Circulars, 1890.
‖ Salvioni, *Rend. della R. Acad. del Lincei*, vol. v. fasc. 7.

And then we find as the values of the tubes in Legal Ohms:

	Benoit.	R. T. G. 1891.
37	1·00045	1·00033
39	·99954	·99959

and these numbers show an extremely close agreement, thus proving that the resistance of a column of mercury 100 cm. in length, 1 sq. mm. in section, as given in this indirect way by Benoit's experiments, is very close to the value ·9535 B.A. unit.

In my previous paper * are given some values for the change of resistance of mercury with temperature. On January 3 I observed the resistances of the tubes Nos. 37 and 39 at a temperature of 12°·9 C. The results were:—

	Resistance at 12°·9.
37.....	1·02254
39.....	1·02193

From these we get as the values of the coefficients per 1° C., ·000875 and ·000870 respectively. Thus the mean coefficient between 0° and 13° is ·000872. This agrees well with the values found in 1885, the mean value between 0° and 10° being ·000861, and between 0° and 15° ·000879. From these we have as the value between 0° and 13°, ·000872.

Benoit † and Strecker ‡ give higher values than the above, Strecker's value between 0° and 13° being ·000906.

In the paper on the specific resistance of mercury, Phil. Trans. A, 1888, I have called attention to some of the consequences of this difference. The value of the coefficient between 0° and 10° found by Mr. Fitzpatrick and myself in 1888 was ·000876. Kohlrausch § and Strecker ‖ find as the values for the resistance of mercury in B.A. units, ·95338 and ·95334; these are less than the value found by Salvioni, Hutchinson, Wuilleumeier, and myself, and the difference is, I believe, mainly due to the uncertainty in the temperature coefficient. They both worked with their tubes in a bath at about the temperature of the room, and reduced their results to 0° by the use of Strecker's coefficient. The mean temperature adopted by Kohlrausch was 10°, he puts

$$\sigma_0 = \frac{\sigma_{10}}{1{\cdot}00904},$$

* Phil. Mag. October 1885.

† Benoit, *Journal de Physique*, 1884.

‡ Strecker, Wied. *Annalen*, vol. xxv. p. 475.

§ Kohlrausch, *Abhand. der K. bayer. Akad. der Wiss.* ii. Cl. xvi. Bd. iii. Abt.

‖ Strecker, Wied. *Annalen*, vol. xxv. p. 475.

σ_0 and σ_{10} being the resistances at 0° and 10°. According to my own results in 1888 we should have

$$\sigma_0 = \frac{\sigma_{10}}{1{\cdot}00876};$$

and the value of σ_0 would be increased from ·95334 to about ·95360, which is rather greater than my value. The value ·000876 is given by Benoit for the mean coefficient between 0° and 10°.

XII. *On the Mutual Solubility of Salts in Water.* *By* J. E. Trevor *.

INTEREST in this problem has been again aroused by a new investigation by Dr. W. W. J. Nicol †, in which is presented a review of the older literature, together with new solubility determinations and a series of interpolation formulæ to express the results. Inasmuch as no mention is made of the recent investigations which have shed so much light upon this hitherto dark subject, I take this opportunity to call attention to the solidly grounded explanations which characterize the more recent progress in the study of the complicated phenomena which are here presented.

That the addition of a salt to the saturated solution of another sometimes increases, sometimes diminishes the solubility of the latter, has been long known. The explanation was first given in 1889 by Nernst ‡, in a simple application of the famous Law of Mass Action § to the conditions of electrolytic dissociation shown by Arrhenius ‖ to exist in aqueous solutions of electrolytes, to which class of bodies the inorganic salts belong. This theory, as is well known, indicates the necessity for assuming the dissociation of a certain portion of the dissolved electrolyte into its ions, and is intimately connected with the van't Hoff theory of osmotic pressure ¶, which shows the entire analogy between the conditions of bodies in gaseous form and in solution. The undissociated dissolved molecules and the dissociated ions produce the same pressure effects as the undissociated and dissociated molecules of a gas. Direct application of the laws of gases explains the

* Communicated by the Author.
† Phil. Mag. 1891, xxxi. p. 369.
‡ Nernst, *Zeitschrift für phys. Chemie*, iv. p. 372.
§ Theory of Guldberg and Waage.
‖ Arrhenius, *Zeitschr. für phys. Chem.* i. p. 631.
¶ Van't Hoff, *Zeitschr. für phys. Chem.* i. p. 481.

phenomena of solution. If to a saturated volume of a partially dissociated gas be added one of its gaseous dissociation products, as for example NH_3 to dissociated NH_4Cl vapour, the partial pressures of this constituent are added together and the dissociation is decreased, solid ammonium chloride is precipitated. An indifferent gas, as nitrogen, produces no such effect. In the same way, if one of the dissociated ions be added to the saturated solution of a dissociated salt, the dissociation will decrease and solid salt will be precipitated. For example, in Dr. Nicol's experiment with the chlorides: in KCl solution a considerable proportion of the salt molecules are dissociated into K and Cl ions. Cl ions alone cannot be added to the solution; addition of NaCl, however, adds Cl ions, together with an equivalent amount of Na ions, which latter act indifferently, just as the nitrogen in the case of dissociated ammonium chloride. The partial (osmotic) pressure of these Cl ions is added to that of those already present and solid salt is precipitated, the solubility of the KCl is decreased.

This consideration applies generally to cases of the mutual influence of dissociated bodies with a common ion upon the solubilities of one another, including Dr. Nicol's "Fresh field of investigation" in determining the solubilities of one salt in solutions of various degrees of concentration of another. The requirements of the theory have been shown by Nernst * and Noyes † to hold *quantitatively* in cases of rather slightly soluble substances, as, for example, *a* Brom-iso-cinnamic acid with oxanilic acid, $AgBrO_3$ with $AgNO_3$ and $KBrO_3$, and many more. In the cases of very soluble salts, where the osmotic pressure is measured by hundreds of atmospheres, the question becomes far more complicated, owing to the serious variations from the simple laws of gases, which are manifested at such high pressures in solutions as well as in gases proper. For this reason it is impossible to calculate quantitatively the results in the cases which Dr. Nicol has given, yet without the simple explanation which the above-mentioned recent researches have made clear, the phenomena would be entirely unintelligible, for in the case of any pair of salts it could not be foreseen whether an increase or decrease of mutual solubility would take place. A continuation of this line of work has brought a simple explanation of those anomalous cases where the solubility of an electrolyte is increased by the addition of a dissociated body with a common ion. A striking example is the strong increase in the solu-

* Nernst, *Zeitschr. für phys. Chem.* iv. p. 372.
† Noyes, *Zeitschr. für phys. Chem.* vi. p. 241.

bility of mercuric chloride ($HgCl_2$) caused by the addition of hydrochloric acid (with the common Cl ion) to the solution. For this and a number of allied cases the explanation has been shown by Le Blanc and Noyes* to lie in the combination of $HgCl_2$ and HCl to form double molecules, a different substance with a different solubility. The determinations were made by observation of the freezing-points of the solutions, the lowering of the freezing-point being, as has been shown by Raoult and others †, a function of the number of molecules (or free ions) in the solution.

Further work in this same direction ‡ has applied, with quantitative results, the Law of Mass Action to cases of the mutual influence of the solubilities of pairs of salts which do not possess a common ion. This work is of extraordinary interest, since without the above indicated theoretical explanation the observed phenomena would seem entirely without meaning, the results could not in any way be foreseen. The possibility of *quantitative* experiment is in this entire field limited only by such concentrations which produce an osmotic pressure in the solution not so great that the laws of gases no longer hold.

That these results already obtained agree over such a range as that including inorganic salts and organic acids is strong evidence for the soundness of the assumptions upon which the work is based, more especially so since, so far as my information goes, no other explanation whatever has been able to account for the facts.

It will be of interest to state that the above developed considerations explain the action of a method used by Dr. Nicol in purifying the chlorides and nitrates used by him, that of precipitating the former by hydrochloric acid and the latter by nitric acid. In this case the common ion Cl or NO_3 added decreases, in the way explained, the solubility of the salt, which is consequently precipitated. In the same way, to increase the insolubility of a precipitate a little sulphuric acid is by analysts added to the wash-water in washing out lead sulphate, or, in general, an addition of some of the precipitating reagent to increase the insolubility of a precipitate.

As bearing upon this question I take the opportunity to communicate some results recently obtained by me § in a case of mutual solubility where the formation of a double salt is

* Le Blanc and Noyes, *Zeitschr. für phys. Chem.* vi. p. 385.

† Raoult, *Ann. chim. phys.* [6] ii. p. 66; also Arrhenius, *Zeitschr. für phys. Chem.* i. p. 647.

‡ Noyes, *Zeitschr. für phys. Chem.* vi. p. 262.

§ Trevor, *Zeitschr. für phys. Chem.* vii. p. 468.

possible. The salts chosen were the sulphates of potassium and copper, from whose common solution the well-known double salt $K_2Cu(SO_4)_2.6H_2O$ is easily obtained. That the components were not, at least to an appreciable extent, combined to double molecules in the concentrated solution of the double salt, was shown by the possibility of separating them by diffusion ; and the interesting fact was further brought out, that a saturated solution of the two salts together was possible, in which both were present in the approximate ratio of their separate solubilities; this condition of solution was, however, rendered unstable by the tendency of the more insoluble double salt to crystallize out. This result had been already foreseen and theoretically explained by Ostwald *. It was further shown that either salt, added in solid form, will not drive the other entirely out of its saturated solution, as had been maintained by Rüdorff, but that in each case a definite state of equilibrium occurs where the solution is not changed by further additions. These equilibria are the same whether the salts be added each to the saturated solution of the other, or directly to that of the double salt.

By such investigations as the one just quoted, by means of diffusion, and more particularly by the method of determination of the lowering of the freezing-point of solutions, made use of by Le Blanc and Noyes, are the answers brought to the objection of Dr. Nicol that we cannot tell whether the double molecules be formed in the solution or only at the moment of separation of the solid salt.

To answer this objection it is not even necessary to assume the electrolytic dissociation; the simple fact shown by Rüdorff, whose work Dr. Nicol quotes, that from saturated double salt-solutions the constituent salts may be separated by diffusion, demonstrates that the double molecules cannot to an appreciable extent be present.

The main question, however, that of reciprocal solubilities, has, as I have endeavoured to point out, already been answered. The extension of the theory *quantitatively* to concentrated solutions of very soluble salts is seriously complicated by the variations from the simple laws of gases which occur with the high osmotic pressures there found, and this extension must come from a study of these variations and not from the building up of interpolation formulæ to represent solubilities.

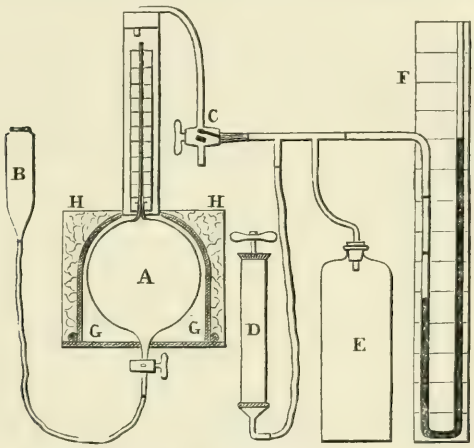
University Laboratory of Physical Chemistry,
Leipsic, Germany, May 1891.

---

* Ostwald, *Allgemeine Chemie,* 2 Auf. vol. i. pp. 1076–1078.

XIII. *An Apparatus for Measuring the Compressibility of Liquids.* *By* S. Skinner, *M.A., Demonstrator at the Cavendish Laboratory, Cambridge*.*

THE special features of the apparatus are (*a*) its very large bulb, (*b*) an arrangement to facilitate the filling and emptying processes. The volume of the globe is 1300 cubic centimetres, so that a small alteration of pressure, such as half an atmosphere, produces a considerable movement of the index in the capillary tube of which the capacity per cm. is ·003 cubic centim. To facilitate the introduction of liquids a second tube, closed by a stop-cock, is sealed in at the lower



portion of the globe, and this is connected by a rubber-tube with a side reservoir. If a liquid be poured in the reservoir and the stop-cock be opened, the liquid will flow into the globe. The apparatus is supported on a base-board through which the tube carrying the stop-cock passes. A bell-jar stands on the base-board and is in connexion with a condensing air-pump and a mercurial pressure-gauge.

The behaviour of the apparatus has been tested by using it for a determination of the compressibility of water, with the following results :—

	Found.	Calculated from Tait's Extrapolation Formula.
At 5°·45 C.	·0000510	·0000502
9°·4.....	·0000501	·0000488
12°·4.....	·0000485	·0000479
16°·2.....	·0000480	·0000468

* Communicated by the Physical Society : read May 9, 1891.

The apparatus has been applied to the comparison of the compressibility of solutions with that of the solvents, and the results exhibit the same general relations as with other properties of solutions. The solutions divide themselves into two classes, which may be broadly termed electrolytic and non-electrolytic. In the first there is a very considerable decrease in compressibility, as much as 8 per cent. with a 3-per-cent. solution of NaCl; whilst in the second there is but a slight diminution, quite beyond the limits of accuracy of the apparatus. For instance, a 5-per-cent. solution of naphthalene has a diminution of under 1 per cent.

A strict interpretation of the theory of osmotic pressure in solutions has been made by Prof. J. J. Thomson, in his "Applications of Dynamics to Physics and Chemistry," § 97, where he finds that 1 gram-equivalent per litre would decrease the compressibility by 1 part in a thousand. Non-electrolytes in dilute solution appear to follow this law; this is in agreement with their other properties, such as alteration in boiling- or freezing-points.

The diagram will serve to explain the general arrangement of the apparatus.

XIV. *The Influence the Size of the Reflector exerts in "Hertz's Experiment."* *By* Fred. T. Trouton*.

OWING to the requirements of certain refraction experiments in which I was engaged, it became necessary to investigate more fully than had been previously done† the influence the size of the reflector has in determining the position of the nodes in Hertz's now well-known electromagnetic interference experiment.

Radiation of a suitable period was produced by Hertz for this experiment, as is well known, by taking advantage of the alternating character of the discharge of an electric condenser. For this purpose two similar conductors, generally speaking two brass cylinders, are placed together end to end with a spark-gap between them, and are charged by an induction-coil, with the poles of which they are connected. The rapidly alternating current which occurs between them at each discharge originates electromagnetic waves which spread out into space. In these waves the electric component is parallel to the common axis of the cylinders, while the magnetic component lies at right angles.

* Communicated by the Author.

† 'Nature,' Aug. 22nd, 1889.

We can now detect these waves in a variety of ways. Hertz employed in his interference experiments a simple circle of wire interrupted at one place by a short gap, the wire being of such a length that the period of electric oscillations from end to end on it is the same as that of the radiation with which it is to be used, so that the currents induced in the wire by a series of waves are synchronously reinforced until the ends, always oppositely charged, overflow, and a spark occurs.

By means of perpendicular reflexion from a metallic sheet a beam of the same period travelling in the opposite direction is obtained which will interfere with the direct one, and a series of loops and nodes result, just as in an organ-pipe. The position of these nodes Hertz detected by the use of the resonating receiver, the nodes and loops being distinguished by the variation in the intensity of the sparking across the gap as the distance of the resonator from the reflector was changed. The magnetic and electric forces in these stationary waves are everywhere complementary, that is, where one is a maximum the other is a minimum. The first magnetic node or place of minimum intensity of that force is situated at one quarter the wave-length from the reflecting sheet, and so on for the others, in the usual sequence of loops and nodes.

Some time since I observed that the distance of the nodes from the reflector was influenced by its size, and a short account was given in a paper in 'Nature,' vol. xl. p. 399, but until the present no determinations were described systematically made with various sized reflectors.

When a number of square sheets of various sizes were tried as reflectors, it was found that as the sheet became smaller the distance of the node from the sheet became greater. The increase seemed to tend towards becoming one eighth of the wave-length as the size of the reflector diminished, but with small sheets the intensity of the reflexion is very slight, and so it soon becomes impossible to make any satisfactory determination.

Perhaps the most noticeable thing in connexion with reflexion from sheets of limited size is the great difference in the effect, where the sheet is rectangular in shape, according as its long dimension is parallel to the direction of the magnetic or electric component of the incident wave. This undoubtedly is connected with the accumulation of charge on its edges, according as they lie in the direction suitable for it or not. A long narrow strip (say anywhere between one quarter and one half the wave-length in width) held with its

length parallel to the magnetic direction, has the node nearly as far out as if it were a square. But with the same strip held at right angles, parallel to the electric direction, the node is practically at one quarter the wave-length, just as it would be for an infinite sheet.

It was thought desirable, in making the experiments, to use long strips for reflectors, as being a somewhat simpler case than square plates. In the present determinations the position of the node was found for a number of long strips of regularly increasing widths, first, when the long dimension of the reflector was held in the direction of the magnetic component, in which case the great shifting outwards of the node occurs; and, secondly, when held at right angles, or in the electric direction, in which case there is generally little or no effect to be found.

Nothing further as to the character of the effect than had been previously observed was noticeable in the first case; but in the second case, that is where the length of the strip is held in the electric direction, a distinct peculiarity was found when the strip was very narrow. It may be remarked that good reflexion can be obtained from strips in the second case quite too narrow to afford reflexion when held at right angles in the magnetic direction as in the first set. And it is with these very narrow strips that the peculiarity is noticed. The node, which until the strip is very narrow is practically unaffected by the width of the strip, is now situated *nearer* the reflector than one quarter the wave-length. This has considerable interest attached to it because it was really observed by Hertz in his original experiments, though he attributed it accidentally to quite another cause.

The vibrator or source of radiation employed in the following experiments consisted of two brass cylinders with rounded gilt ends (about 13 cm. long and 3 cm. in diameter), placed near each other in the focal line of a cylindrical parabolic mirror so as to give a parallel beam. It afforded radiation containing waves of a variety of periods*, but that selected by the "resonator" employed had a wave-length of 68 cm. The resonator, which was of the circular type, was placed in the centre of the beam at about 2 m. from the vibrator, in front of the metallic sheet used as reflector. It was always held so as to receive the magnetic component only, that is in the plane containing the axis of the vibrator, and with the diameter of the circle through the spark-gap parallel to this axis; in this position, only the magnetic lines of force can take effect. Thus throughout the following the magnetic force alone is

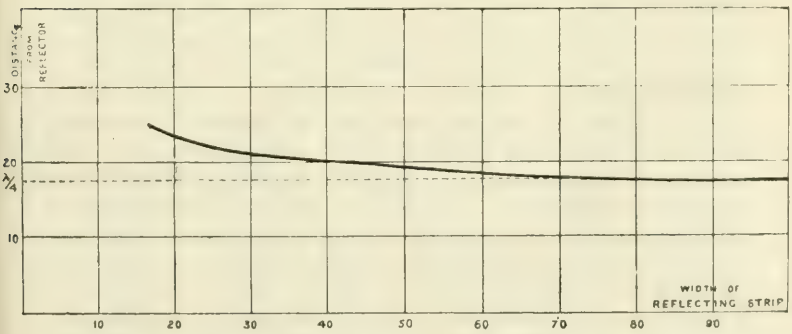
* 'Nature,' vol. xli. p. 295.

dealt with, and so, in speaking of the nodes, the places of minimum magnetic force alone are meant.

Care was taken, when determining the wave-length, to have as reflector a sheet sufficiently large so that no increase in size could produce any change in the distance of the nodes from it. When this is the case, it may be considered infinite in extent. The large sheet was then replaced in turn by smaller sheets, and the position of the node in each case observed. The experiments, as mentioned before, divide themselves into two parts. First, where an infinite reflector is, so to speak, gradually shortened in the direction of the electric component of the wave, but remains unaltered at right angles, whilst the accompanying change, if any, in the position of the node is observed; and, second, when the shortening takes place in the direction of the magnetic component.

The general results of the first set of experiments are seen at a glance by means of fig. 1. The abscissæ here represent the length of the reflector in the direction of the electric component, while the ordinates represent on the same scale corresponding to each sized reflector the distance of the resonator from the reflector when placed in the first position of minimum sparking. The length of the reflector in the direction of the magnetic component was 90 cm., as that was found to be amply sufficient, *i. e.* increase was found to produce no effect. The resonator was held in front of the centre of the reflector.

Fig. 1.



It will be seen from the curve that when the reflector is less than a wave-length the node begins to be shifted sensibly outwards from the true quarter wave-length position, so that to avoid these diffraction-effects mirrors should be at least a wave-length in the electric direction.

The following table served for plotting the curve. In the first column are the dimensions of the reflector in the direction of the electric component. Six determinations were made of the position of the node with each sized reflector. The mean of these is given in the last column. The reading taken was in each case the nearest quarter centimetre, the nature of the observations making further exactitude unnecessary. The effect from a 12 cm. reflector was too weak to admit of an observation.

TABLE I.

16	24¾	23¾	22½	24¾	24½	24¾	24·2
20	22	22½	23¼	22½	22¾	22¼	22·5
24	21	22¼	22¾	21½	21¾	21¾	21·8
28	21¾	20½	21¾	21¼	20¾	21½	21·2
32	20¼	20½	21¼	21½	20½	20½	20·7
36	20½	20	20¾	21	20½	20½	20·5
48	19	19¼	19½	18¾	18½	18½	18·9
60	17¾	18	18¼	18½	18¼	17½	18
75	17	17	17	16¾	17¾	17½	17·2
Large sheet	17¾	16¼	17¼	17	16¾	17¼	17

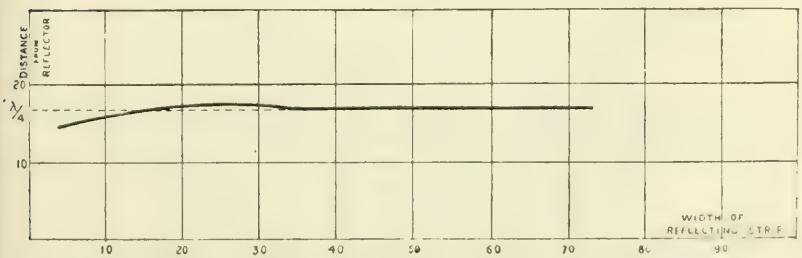
The effect produced in the reflected wave by shortening the reflector in the direction of the electric component can be considered equivalent to an acceleration or change of phase on reflexion. This equivalent change of phase is at least double that corresponding to the distance the node is shifted, because of the double journey back and forwards which the reflected wave has to make. But the complete change in phase must be really greater than this, for it is to be remarked that the node observed in these experiments is peculiar, and differs from that ordinarily considered where two non-divergent beams travelling in opposite directions interfere. The beam reflected from a small reflector is divergent, and consequently diminishes rapidly in intensity on proceeding outwards. This causes the node or minimum sparking-position to be a little nearer the reflector than the true position of opposite phase. The intensity of the reflected vibration at this point, before it can be subtracted from the incident one, has no doubt to be diminished in proportion to the cosine of the difference in phase between them; but this is more than made up for by the increase in intensity due to its nearer position, so that the approximation towards complete interference is better here than at the true phasial position. That the interference, then, is comparatively slight is seen by the fact that with the smaller sized reflectors it is

always easy, by diminishing the sparking-gap, to obtain sparking in the minimum position; this is not possible when large sheets are employed as reflectors.

Without being able to calculate in the case of a given sized reflector what the amount of the equivalent acceleration in phase should be, it can be seen that there should be a difference in phase between the current induced in the reflector and the incident wave when the reflector is short in the electric direction. For the edges afford a capacity and become charged each vibration, the charges opposing the inducing electromotive force, so that the effective electromotive force will reach its zero value sooner than when there are no edges for the accumulation of charge.

The problem of finding the reflexion from a reflector of limited size presents considerable difficulties. An approximation, however, has been obtained by the author* by taking advantage of Hertz's solution in the case of his "vibrator." The short reflector is assumed equivalent to another vibrator, and Hertz's equations of the wave are found for it, by making the total magnetic force due to both primary and secondary vibrator behind the sheet zero. This necessitates assuming that the reflexion comes from the central part only. This condition renders it very limited in its application; nevertheless calculation made by it of the position of the node shows it displaced at all events in the right direction, and to an extent comparable with observation. This method leads naturally to looking at the cause of the displacement, from the point of view of an increased velocity of the wave in the neighbourhood of the reflector, for so it appears in Hertz's theory of his "vibrator."

Fig. 2.



In the second set of experiments the narrowing of the reflector is in the magnetic direction. It will be seen from the curve, fig. 2, plotted from the results, that the large outward

* Phil. Mag. March 1890.

displacement of the node or minimum sparking-position is absent in this case.

On reaching comparatively small dimensions the inward shifting of the node takes place. This is probably best attributed not to a change in phase on reflexion or diminution in velocity in transit, but to the fact that the beam is rapidly diminishing in intensity on passing outward from the reflector, and, as mentioned before, the minimum sparking-position is a compromise between the phase and the intensity.

It might be thought that this action would never displace the node by a sensible amount, but the following consideration shows this not to be so. Let

$$y_1 = \sin 2\pi\left(\frac{t}{\tau} + \frac{x}{\lambda}\right),$$

where x is distance measured from the reflector, represent the incident wave; and let us make some assumption as to the rate the intensity of the reflected disturbance diminishes as the distance increases. Of several tried, that which happened to give results most nearly in agreement with the observations assumed the amplitude to diminish as the square of the distance from a point situated behind the reflector at a distance equal to its width. In this case, calling the width b, we have as the reflected wave

$$y_2 = \left(\frac{b}{b+x}\right)^2 \sin 2\pi\left(\frac{t}{\tau} - \frac{x}{\lambda}\right).$$

On addition the stationary wave is determined by

$$y_1 + y_2 = \mathrm{A} \sin 2\pi\left(\frac{t}{\tau} + \phi\right),$$

where

$$\mathrm{A}^2 = 1 + \left(\frac{b}{b+x}\right)^4 + 2\left(\frac{b}{b+x}\right)^2 \cos 4\pi\frac{x}{\lambda}.$$

Differentiating and equating to zero as being the condition for a minimum, we find the position of the node to be given by

$$\left(\frac{b}{b+x}\right)^2 + (b+x)\frac{2\pi}{\lambda} \sin 4\pi\frac{x}{\lambda} + \cos 4\pi\frac{x}{\lambda} = 0.$$

When b, the width of the reflecting sheet, is taken as 4 cm., this equation requires x to have the value of about 14·3. That means a shifting inwards of the node by 2·7 cm., which is a little more than is required to correspond with observation, the nodal position given in Table II. for a 4 cm. sheet being at 14·6 cm. from the reflector.

If the amplitude of the reflected beam be taken simply as $\frac{b}{b+x}$, instead of its square, a somewhat more natural assumption, the value found for x is about 15·8—which is a shifting inwards considerable in deficit. It is thus evident that, apart from other considerations, a rapid falling-off in the intensity of the reflected disturbance is quite competent to effect an appreciable inward displacement of the node. However, it must be remembered that in cases like the present, where the intensity of one component changes rapidly with the distance, the minimum sparking-position must only be considered as a kind of *pseudonode*, not a true phasial one.

Taking a long shaped strip of zinc about 20 cm. wide, the experiment alluded to above, one somewhat analogous to Stokes's 'Experimentum Crucis,' is easily made. The position of the node when the strip is stretched in the electric direction, that is with its small dimension in the magnetic, will be found to be distant about one quarter the wave-length, much the same as with an infinite sheet: but on rotating the strip through 90° into the magnetic direction the node will be displaced outward, showing clearly the dependency of the effect on the two directions.

In Table II. are given the results of the experiments from which the second curve was plotted. In the first column are the dimensions of the reflector in the direction of the magnetic component. The mean of the four determinations with each sized reflector is given in the last column.

Table II.

4	14¾	14¼	15½	14¼	14·6
8	15¼	14½	16¼	15¼	15·3
12	16½	16¼	16¼	16½	16·4
20	17½	17	17¼	16½	17
24	17	17½	17¼	17¼	17·2
28	17½	18	17¼	17½	17·6
32	18	17¼	17	17¾	17·5
36	16¾	17	17½	17¼	17·1
48	16¾	17½	16½	17¼	17
Large sheet	16½	17	17½	16¾	16·9

It will be seen that it was possible to obtain determinations with much narrower reflectors in the present experiments than was previously found possible when dealing with the strips held so as to be short in the electric direction. Thus a given sized strip evidently must reflect less strongly when held so that its longest edge is the one which becomes charged

each oscillation, that is to say, with this edge at right angles to the electric component. And, indeed, this is as we should expect, since on comparison we see that in this case there is less area which can act effectively as a source of reflexion through the passage on it of current each oscillation. For all the electricity of course does not go to the very edge, but there is gradual accumulation of charge over the surface approaching the edge, increasing no doubt up to it. Consequently the current diminishes in intensity towards the edges, and thus it is only those parts of the reflector remote from the charged edges which can be considered completely effective in producing the magnetic component of the reflected beam. Each centimetre of charged edge, so to speak, reduces the effective area of a reflector, so that with a rectangular sheet strongest reflexion is obtained when the edge charged is shortest.

A very slight increase in the nodal distance is seen by the table to occur when the reflector is somewhat less than half a wave-length wide; this may require further experiments of a more sensitive character before being finally accepted. If it be the case, it would seem as if there were really an acceleration of phase on reflexion from mirrors small in the magnetic direction also, but so slight as to be almost entirely masked by the inward tendency due to divergency in the reflected beam. If we look at it from a purely optical point of view, Fresnel's theory indeed represents a linear reflector as having an acceleration of phase of $\frac{1}{8}\pi$; however, this is omitting all considerations of direction in the vibration; but we have seen that the whole phenomenon requires a treatment introducing a difference depending upon the magnetic and electric directions. An acceleration of $\frac{1}{8}\pi$ might suit very well in the magnetic case, but it is certainly insufficient when the reflector is narrow in the electric direction, as is seen from Table I. With a quarter wave-length of 17 cm., the effect of a change in phase of $\frac{1}{8}\pi$ on reflexion would be to shift the node out to 21·25 cm., that is out through $\frac{1}{16}$ the wave-length; but this is seen by the Table to be much too little, especially so when we remember that the observed minimum sparking-position must always be somewhat nearer the reflector on account of the divergency effect than the true position of opposite phases.

The result of diminishing the reflecting sheet simultaneously in both directions was also examined, but though it was very evident that the reduced dimension in each direction tended towards possessing its own respective effect, no simple relation between them exhibited itself; thus with a reflector

24 cm. square, the node was found at 22·4 cm., a little further than 21·8, which it is at when the sheet is long in the magnetic direction (Table I.), and this is as it should be, shifted out owing to both. Again, a reflector 24 cm. in the electric direction, and 10 cm. in the magnetic, had a node at 21·5 cm., a little less than with a long sheet, and this also is in the direction to be anticipated. Some few other experiments were made, but in the absence of a workable theory for the whole phenomenon, it was thought undesirable to pursue the matter further at present.

An interesting point arises in connexion with those experiments made with the reflector narrow in the magnetic direction, in which an inward shifting of the node was observed. In Hertz's original determinations he found that the first node was situated not quite so much as $\frac{1}{4}$ the wave-length from the reflector. He attributed this to imperfect reflexion arising from imperfect conductivity in the material of his reflector, which was a large sandstone wall with a number of gas-pipes across it, and had on it besides to increase the effect a zinc sheet 2 m. long in the magnetic direction and 4 m. long in the electric; there were also wires attached to the ends of the sheet for leading off the charges, so that it must have been equivalent to a much longer one in the electric direction. Now it seems probable that the sheet was sensibly the only thing that reflected, and that the inward displacement was really due to its comparatively small size in the magnetic direction, for the wave-length he employed was nearly 10 m., so that the reflector was about $\frac{1}{5}$ the wave-length in width. This corresponds to about a 14 cm. mirror with a wave-length of 68 cm.

Hertz found the inward displacement correspondingly greater than is given in Table II., but his incident beam must have been divergent, as he worked nearer the vibrator in proportion to the wave-length, while my beam was rendered fairly parallel by the parabolic mirror employed.

To make quite sure that in reflexion off a large sheet the first nodal distance 17 cm. was really one quarter the wave-length, the position of the second node was redetermined and found to be distanced from the reflector about 51 cm.—the mean of five determinations*. The vibrator in these experiments was over three wave-lengths away from the reflector.

It is very convenient, in carrying out these experiments, to have an arrangement for moving the resonator backwards and forwards a known amount. A simple arrangement for effecting this is to support the resonator at one end of a rod

* 2nd node.. ‖ $49\frac{3}{4}$ | $51\frac{3}{4}$ | $50\frac{1}{2}$ | 50 | 51 ‖ 50·6

pivoted in the middle, and kept vertical by a weight attached to the other end. By means of two screw-stops the excursion to either side of the vertical position is limited to any desired amount. The method of procedure in identifying a node is, then, to find a position for the resonator such that on moving it an equal amount to either side, sparking just takes place. This can of course be done with facility in a darkened room.

When possible, it is still more convenient to move the reflector backwards and forwards a known amount, instead of moving the resonator, and the node is found similarly to before as the position where sparking just occurs in the extreme position of the reflector; this admits of being done when the reflector is small. The reflector was suspended by vertical cords about 3 m. long, and could be thus moved backwards and forwards practically parallel to itself with the greatest ease even in the dark, the amount of the movement being limited by stops. The advantage of this arrangement is that the adjustment of the resonator is unaffected, for when it is the resonator that is moved the disturbance is very liable to alter the spark-gap.

I have much pleasure here in thanking Prof. Fitzgerald for his advice and material encouragement on many occasions throughout the investigation.

Note.—Since sending off to the printers' I have learnt that MM. Sarasin and De la Rive (Phil. Mag. June 1891) have, unlike Hertz, observed no inward displacement of the node towards the reflector. Their experiments are quite in agreement with the explanation given above, for their reflector was about a wave-length in the direction of the magnetic component.

XV. Mr. Sydney Lupton's *Method of Reducing the Results of Experiments*. *By* Spencer Umfreville Pickering, *M.A., F.R.S.**

THE conclusions which I drew from an examination of various properties of sulphuric-acid solutions (Chem. Soc. Trans. 1890, pp. 64 and 331; Phil. Mag. xxix. p. 427) have recently been made the subject of an adverse criticism by Mr. Sydney Lupton in the pages of this Magazine (vol. xxxi. p. 418).

* Communicated by the Author,

The properties examined by me were the heat of dissolution, electric conductivity, heat capacity, freezing-point, densities (4 sets of determinations at different temperatures), contraction on mixing and expansion by heat (for 3 different intervals of temperature); and, as I repeatedly insisted, the whole strength of my conclusions rested on the fact that all these different properties, forming figures differing so entirely, as they did, from each other in general appearance (see Phil. Mag. xxix. pp. 430, 431), yet indicated the existence of changes of curvature at the *same* points. The indications were obtained by examining both the experimental figures, and also the curves representing the rate of change of the properties with change of composition (the direct first differential), with the help of a bent ruler; totally different methods of plotting, moreover, were adopted, without in any way modifying the conclusions drawn, and these conclusions were further strengthened by the fact that the various sections in which the whole figures have to be drawn all appeared to be curves of a similar nature—parabolas of a certain order—as was proved by their yielding straight lines on further differentiation, and also by the fact that these changes, wherever it was possible to draw any conclusion at all on this head, occurred at simple molecular proportions of the acid and water.

Thus the main feature of the evidence on which I relied was its cumulative character, and this Mr. Lupton seems to have entirely ignored. My determinations numbered 1100; of these he has examined 10: the indications of changes of curvature numbered 102*; of these he has examined one, and by disproving this one he thinks he will discredit the whole work.

This being the character of my work and of the criticism levelled against it, it is rather surprising to find Mr. Lupton opening his remarks with the following sentence:—"In the hurry of modern life experimentalists are apt to omit the test of accuracy afforded by obtaining the same results by several different methods. Thus long rows of figures are frequently given which have in reality no experimental basis to rest upon."

I scarcely think that I shall be unfair if I accuse Mr. Lupton of attacking my work before he has made himself master of the description of it. He complains of the absence of those very details which he might have found by looking

* Not, however, at 102 *different* percentages, as Professor Armstrong imagines (see Chem. Soc. Proc. 1891, p. 106).

through my papers: he raises numerous minor objections, nearly all of which I have fully answered, and his chief weapon of offence is the representation of a small portion of one of the sets of my density results by a parabola deduced mathematically, and which, if strictly applicable, would negative the existence of one of the changes of curvature which I considered probable, in ignorance of the fact that I myself had applied the same method of examination to the same portion of all but the same curve, and had shown why the results obtained did *not* negative the existence of the change in question (Chem. Soc. Trans. 1890, p. 78). From this examination Mr. Lupton arrives at a similar provisional conclusion to what I did, "if the limits of accuracy are $\frac{1}{50000}$," then this small portion of this series of my "results can be expressed by a single curve." But, apparently, "the hurry of modern life" prevented Mr. Lupton from ascertaining whether the experimental error *was* $\frac{1}{50000}$, and whether, therefore, this result led to any argument against my conclusions. But $\frac{1}{50000}$ is a somewhat large quantity when it refers to the weight of 25 c.c. of strong sulphuric-acid solutions; it is about 8 milligrams; and had Mr. Lupton taken the trouble to ascertain from the numerous values available for this purpose (Trans. 1890, pp. 70, 71; Phil. Mag. xxx. p. 402) what the probable experimental error really was, he would have found that it was *not* $\frac{1}{50000}$, *not* $\frac{1}{500000}$, and scarcely even $\frac{1}{5000000}$.

As Mr. Lupton's argument depends entirely on the concordance between the values calculated from his equation and the experimental values, it was certainly incumbent on him to make sure that his calculations were correct; but this he did not do, and of the two errors which he made one was a very important one*. I therefore take the liberty of giving the following amended version of the first and last columns of his table, in which x is the percentage strength of the solution, and u calc. $-$ u obs. the differences between the actual densities and those calculated according to Mr. Lupton's equation, which represents these results as forming one continuous parabolic curve. In two cases only out of the 10 results which Mr. Lupton investigated (50 to 68 per cent.) does the difference even approach to $\frac{1}{50000}$, while the average difference is $\frac{1}{10000}$, that is 50 times greater than the probable error mentioned above, and 23 times greater than the liberal maximum which I allowed as, and also found to be, the limit of error in the majority of cases (Chem. Soc. Trans. 1890, p. 71); but, independently of this, the arrangement of the

* $-\cdot000098$ for $+\cdot000218$ in the last column.

differences of like signs into separate groups would show quite clearly to the most superficial observer that all agreement between the calculated and observed values is absent.

x.	u calc. $-u$ obs.
45·71655	−·000717*
48·02648	−·000404*
50·06998	−·000139
52·02681	+·000038
54·00142	+·000218
56·00914	+·000274
57·85589	+·000299
(59·97052	+·000037)
(61·91205	+·000159)
64·04535	−·000158
66·02517	−·000257
68·00851	−·000278
69·93139	−·000187*
72·02232	+·000008*
73·98643	+·000597

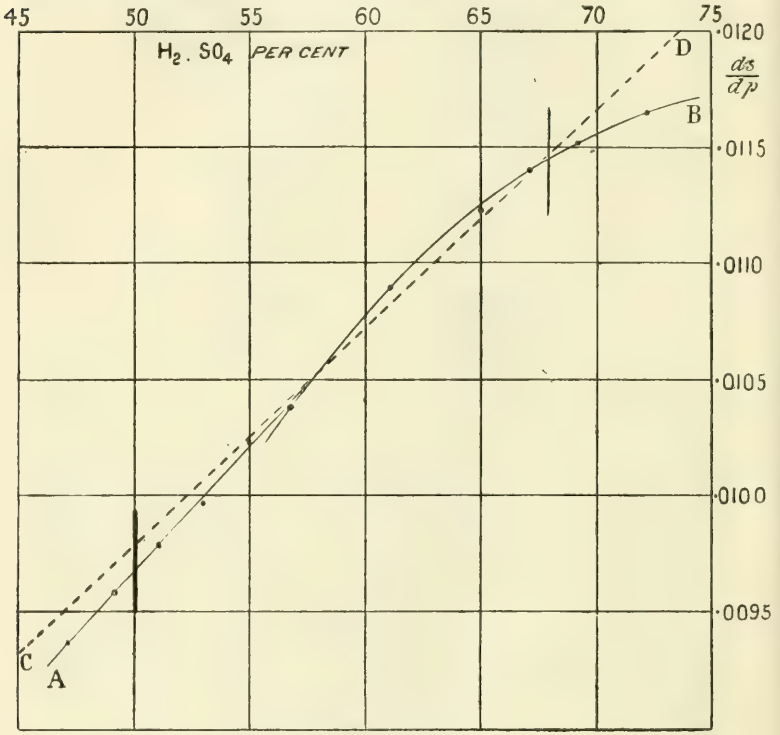
In the above table Mr. Lupton has, somewhat unfairly, included two results (those in brackets), which, as I pointed out (Chem. Trnas.) p. 70, table ii. p. 43, and plate 2 †), were evidently erroneous ; it is immaterial, however, whether they are inserted in the above table or not ; but I have omitted them in the following sketch (p. 94), which gives a far more striking illustration of the untenable nature of Mr. Lupton's contention that "the equation expresses the results with far greater accuracy than could be attained by even the most careful drawing." As the densities themselves are unmanageable for diagrammatic purposes, I have had to take the differentials deduced directly from them.

It is certainly extraordinary that Mr. Lupton should have imagined that he could disprove by such means not only the one particular break in question, but also the 101 others described in my paper, and most of which were far better marked than this particular one. Indeed, it is by some strange accident that Mr. Lupton was led to attack the only one

* These values are not given in Mr. Lupton's table.

† The tables (*loc. cit.*), not the plates, must be taken as giving the correct values. The cross in plate 2 at 62 per cent. is misplaced, and should stand for the three differential points in its neighbourhood showing the accidentally large errors. In the last column of the table on p. 142 for 52·71 read 53·01, and for 46·65 read 46·87.

break in the density-curves which I mentioned as being "of a very doubtful character;" and it is by a still stranger accident that the only hydrate on which his investigation "seems to throw very grave suspicion," is the very one which actually *does* exist, which has been isolated in the crystalline condition (Chem. Soc. Trans. 1890, p. 339), and to the isolation of which I was led by a reliance on the very method which Mr. Lupton considers to be fallacious and worthless.



AB. Direct first differential of the experimental points, and Pickering's representation of them.
CD. First differential of Lupton's calculated values.

So much for Mr. Lupton's main argument; it remains but to answer the minor objections which he raises.

1. Mr. Lupton (p. 420) is "astonished" to find that I give the composition of the solutions to the fifth decimal place; but, as the relative composition of these solutions was correct to one unit in the fourth place (*loc. cit.* p. 73), I was only following precedent in so doing; surely Mr. Lupton would

not quarrel with me for giving accurate tables merely because the special application made of them did not require the full degree of accuracy attained.

2. Mr. Lupton is then "startled" to find that "in the case of experiments, the whole object of which is extreme accuracy," there is a difference of $\frac{1}{1000}$ on each side of the mean in the eight analyses made of the stock acid*—analyses, by the way, which were *not* my own, and the results of which I did *not* take. But will he tell me how the accuracy of my results would have been affected by a constant error of even $\frac{1}{1000}$ in the strength of all the solutions used? Or how my conclusions would have been affected if, for instance, I had found 58·08 instead of 58·14 per cent. as the position of a change, when, for other reasons, this position could not, as a rule, be correctly ascertained within 0·5 or 1·0 per cent.?

3. Mr. Lupton complains (p. 420) that I have given no details as to my method of drawing curves. I had thought that the details on pp. 68, 69, and 184, *loc. cit.*, would have been sufficient, and the only important omission I appear to have made was that I did not mention that the flexible ruler was held at its extremities, the middle portion only being used for the drawing; but this omission cannot account for Mr. Lupton's extraordinary conclusion, p. 421, that "hence the hydrates of sulphuric acid are apparently made to depend upon the flexibility of the steel lath used." Let Mr. Lupton convince himself of the fallacy of this statement by a little experimentation on the curves depicted above with laths of different flexibility.

4. Mr. Lupton refers to Prof. Lodge's "word of warning" to experimentalists on the over-pressure of formulæ ('Nature,' July 18, 1889; see also my answer, August 8, 1889). It is certainly remarkable that Mr. Lupton should consider that this warning applies to me, who used not a single formula, and not to himself, who is relying entirely on empirical formulæ.

5. In the same way Mr. Lupton refers to Prof. Arrhenius's premature criticism of my work, mentioning with approval that Arrhenius pointed out "that my equations for sulphuric acid required the introduction of nearly sixty constants." Mr. Lupton is apparently in ignorance of my answer to Arrhenius (Phil. Mag. xxix. p. 433), and of the fact that since the time when this answer and the details of my results were published Arrhenius has never made good his criticism. I

* Why does Mr. Lupton make only a partial quotation from my table of analyses (*loc. cit.* p. 72)? And why does he not calculate the probable error of the mean of these analyses? It is only $\frac{8}{10000}$.

need only answer Mr. Lupton, as I did Arrhenius, by challenging him to point out one single equation or one single constant in the whole of my papers.

6. Of the objections which Mr. Lupton considers "impugn the *extreme* accuracy of the experimental results" (p. 425), but which apparently, "even if admitted, do not impugn their *great* accuracy"* (p. 429), the first is, that these results do not agree with those quoted by Mendeléeff†. This is incorrect; I clearly stated that the latter "showed such a very good general concordance with my own results that they may be taken together with these as affording a further illustration of the effect of temperature on the figure" (*loc. cit.* p. 79). It was only in my interpretation of the results that I differed from Mendeléeff; and if Mr. Lupton will but compare together the two figures on page 81, *loc. cit.*, I scarcely think that he will say that I was not justified in doing so, or that the accuracy of my results is impugned by the expression of this difference of opinion.

7. Mr. Lupton alludes to the well-known objections against the piknometer. I have nothing to say in favour of this instrument in its usual imperfect form: the only question worth considering is whether the particular instrument which I used gave correct results or not, and I have given Mr. Lupton ample means for judging for himself on that point. I have shown that the error was less than that which might reasonably be attributed to the errors of the balance and thermometer used, that they were as small as those experienced by the best experimentalists when using a Sprengel tube, and moreover that the actual values which I obtained with water at different temperatures agreed most completely with those of Kopp and Pierre (*loc. cit.* p. 70, and Phil. Mag. xxx. p. 406). It may be worth mentioning that the only one of the well-known objections to the ordinary piknometer which Mr. Lupton cites is a mistaken objection, namely "that the stopper does not go in to exactly the same position when unequally pressed." Such a defect would cause an error which would be greater the greater the density of the liquid used; whereas the reverse is the case, as Mr. Lupton might have ascertained by experiments with a faulty bottle. The real source of inaccuracy in density-bottles is the fact that the imperfect

* The italics are Mr. Lupton's.

† Mr. Lupton quotes me as having said "Mendeléeff's values;" but I was careful to point out that the values used by Mendeléeff were collected from the results of other physicists (pp. 66, 79). It would ill become me to impugn the accuracy of any of Mendeléeff's own determinations.

fitting of the stopper offers other capillary openings besides the legitimate one through the stopper; and this, from its very nature, is a defect which may be absent either through accident or through careful manufacture in a particular bottle.

8. Mr. Lupton then complains that I do "not mention any precaution taken to reduce the flask and weights to their true weights *in vacuo*." The complaint is just, and my only excuse for the omission must be that every text-book on physics contains an account of the necessary "precaution."

9. The next complaint is that I mentioned no precautions taken to remove the air dissolved in the solutions, or that retained between the liquid and the glass. Again Mr. Lupton is right; I mentioned none, and, what is more, I took none, because I did not see how they could be taken without altering the composition of the solution in the one case, or altering the capacity of the bottle by heating it to redness in the other. I did mention, however, that I had satisfied myself that the air contained in the water used was insufficient to affect its density (p. 73), and *à fortiori* it would be insufficient to affect the density of the solutions made with it; while the numerous determinations of the water-contents of the bottle, both after it had been left dry in air for a long time, and also after it had been in continuous use throughout the day, were sufficient to assure me that no appreciable error was introduced by any air-film adhering to the glass.

Mr. Lupton seems to imagine that 25 cubic centim. of a liquid in which ·0007 gram of air is dissolved will weigh ·0007 gram more *per* 25 cubic centim. Matters are not quite so simple as this, for the volume, as well as the weight, is altered by the gas; and if the effect of the air is similar to that of, say, hydrochloric acid, the weight of the 25 cubic centim. would be increased by only ·0001 gram.

10. Mr. Lupton then attacks me for applying the term differentiation to the method which I adopted in analysing curves, on the ground that a true differential (as I pointed out myself on p. 67) is of infinitesimal magnitude. As, however, I explained fully the nature of the process which I adopted (for which there is no proper appellation), the name given to it was a very secondary consideration.

11. Mr. Lupton then says that "the smoothing process applied to my first differential diagram ought, if accurately performed, to get rid of those slight changes in first differences which in the second differences mark changes of curvature, and therefore changes of hydration." But why "ought"? Surely only on the strength of a foregone conclusion that there are no changes of curvature or of hydration. I must ask Mr. Lupton,

just as I asked Prof. Arrhenius (from whom he seems to have borrowed this argument, see Phil. Mag. xxix. p. 429), to explain what he means by "accurate" or "proper" smoothing. Why does he not take the whole of one of my first differential density diagrams, and show how it may be accurately smoothed so as to obliterate all changes of curvature? Surely he cannot think that he has sufficiently illustrated the feasibility of this by taking only a small portion of the most regular part of one of these figures. And even if he does, I scarcely think that any one who glances at the result depicted above (woodcut, p. 94) will consider that he has succeeded in the attempt.

12. Lastly, Mr. Lupton says that I am self-condemned by having dealt with second differences deduced from the smoothed first differential curve, while I admit that the individual determinations through which the smooth curve was drawn are scarcely accurate enough for the direct deduction of second differences. Mr. Lupton has evidently not carefully read p. 123 of my paper. To any one acquainted with physical methods it must seem absurd to state that the mean of a number of determinations, or the straight line or curve drawn through a number of determinations, is not, as a rule, more exact at any given point than are the individual experiments. Mr. Lupton might as well say that no statement could be made as to the inclination of a bank of stones, because the lines drawn between two neighbouring stones showed all sorts of different inclinations.

Mr. Lupton has apparently had little experience in the practical manipulation of series of results; and if I have shown any deficiency in forbearance towards him, I must crave his forgiveness, for he has entered on a task which should have been undertaken in no light mood, and only after a thorough mastery of the results which he proposed to demolish. There are very few who can be expected to enter into the details of work such as that now under discussion, and the majority will consent to be led by the opinion of a critic who has presumably made himself acquainted with the intricacies of the subject, especially when he makes an effective bid for their confidence by a display of whole pages of equations. If, however, Mr. Lupton can for a moment place himself in my position and imagine that he has a thousand and more determinations of a most tedious character, the constant care and unremitting labour of two whole years, which are in danger of being blown to the winds by the breath of a superficial critic, he will forgive me for any warmth of expression which he might at first sight be inclined to resent.

XVI. *A Consideration of some of the Objections raised by* Mr. Lupton* *to* Mr. Pickering's *Methods of reducing Experimental Results. By* Edward Harold Hayes, *M.A., Fellow of New College, Oxford* †.

I FEAR that it may appear very presumptuous in an individual whose work in a chemical laboratory has been confined to the simplest cases of qualitative analysis, and who has had no practice in dealing with any important series of experimental results, to attempt to question the validity of the arguments advanced by an expert like Mr. Lupton. It chances, however, that I have studied with considerable care Mr. Pickering's paper on the Nature of Solutions ‡ ; and have gradually become convinced of the very great value of the methods of dealing with experimental data there described, especially as regards the use of a bent lath in drawing the curves. Mr. Pickering would be the first to admit that mathematics are not a subject in which he is deeply versed, so that there would appear to be a danger lest, on some of the points raised by Mr. Lupton, judgment may be allowed to go by default, and an impression be thereby created that there is something essentially unsound from a mathematical point of view in Mr. Pickering's methods.

When a uniform naturally straight lath is acted upon by a system of coplanar forces, the form of the curve assumed by a portion of it throughout which none of the applied forces act is such that the product of the radius of curvature at any point and the distance of the point from some fixed straight line is constant, provided that the radius of curvature is very great compared with the thickness of the lath §. It immediately follows that the general differential equation of the curve is

$$\frac{d^2y}{dx^2} = \left\{1+\left(\frac{dy}{dx}\right)^2\right\}^{\frac{3}{2}} \left\{lx+my+n\right\}\text{ ‖},$$

which contains three arbitrary constants. Since this is a

* Phil. Mag. May 1891.

† Communicated by the Author.

‡ Journ. Chem. Soc. March 1890.

§ I believe that Mr. Pickering held the lath near its ends, and only used the intermediate portion for drawing his curves. Hence the curves obtained by him fulfil the above condition.

‖ For a discussion of this curve see Minchin's 'Statics,' vol. ii. pp. 203–209. Mr. Pickering is not justified, mathematically speaking, in saying that the bent lath "does not form a curve of any particular nature." This statement, however, is practically equivalent to a recognition of the high degree of generality which the curve possesses.

differential equation of the second order, the equation of the curve (which can be expressed in terms of elliptic integrals) contains five constants. It is therefore of a generality equal to that of the conic

$$ax^2+hxy+by^2+gx+fy=1,$$

or of the curve

$$y=a+bx+cx^2+dx^3+ex^4 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the bent lath therefore we possess a means of drawing a curve through the experimental points, which is of a more general nature than those usually dealt with by arithmetical methods, and in which there can be no abrupt change of curvature, however slight, still less change of direction. To the former change corresponds an abrupt change of direction in the first differential curve, and a breaking up of the second differential curve into two curves which do not meet; to the latter a breaking up of the first differential curve into two curves which do not meet *.

Difficulties of accurate drawing excepted, there appears to be no *à priori* reason why the bent-lath curve should represent the actual facts less faithfully than an equation such as (1) above, the arithmetical treatment of which would be terribly laborious. It is also tolerably obvious that a single equation of this nature would be incapable of representing within the limits of experimental error the results of a single series of Mr. Pickering's experiments (*e. g.* one of the direct first differentials of the densities): so that more than one equation, probably three at the very least if the number of constants in each was five or thereabouts, would have to be employed; and their precise number, as well as their respective ranges, would be a mere matter of individual taste.

If it were possible to divide the experimental results into groups in all sorts of ways, calculate the constants for the equation representing each group, and determine in every case the difference between the observed and calculated values, curves fitting the experimental points as closely, if not more so, than Mr. Pickering's might no doubt be obtained, and most valuable evidence deduced from them as to the presence or absence of breaks † at particular points.

* In the former case $\frac{d^2y}{dx^2}$, in the latter $\frac{dy}{dx}$ is discontinuous.

† The word *break* is used to denote a point at which, in an ideal curve which gives an absolutely correct representation of the facts, the values of one of the differential coefficients of the ordinate with respect to the abscissa either become discontinuous or exhibit a rate of change enormously great as compared with that in the neighbourhood of the point.

But Mr. Lupton has not done this ; and without some such process of trial and error, which might occupy years, it is difficult to see how any evidence bearing on this question of breaks, which is the pivot of the whole controversy, can be obtained by the method which he advocates. If we decide with Mr. Lupton to represent a certain arbitrarily selected series of results by a continuous function, any break which may occur within the range of the function will necessarily be smoothed out. This is "excessive smoothing" * with a vengeance. It seems clear therefore that in any satisfactory investigation as to the real existence of breaks some method differing from that favoured by Mr. Lupton *must* be employed.

Now with a bent lath the process of trial and error alluded to above can be carried out to almost any extent ; *i. e.* any number of continuous curves of great though not excessive generality can be compared with the experimental points until those are discovered which fit best. The test for a break consists not only in the good fitting of the lath throughout each of the two groups formed by several consecutive points on either side of the break, but also in the impossibility of getting it to fit to an extent in harmony with the experimental errors when a group of points is chosen which includes the break. In such a case two different continuous curves meeting at the break must be drawn, if the experimental values are not to be departed from to an unwarrantable extent.

It is obvious that breaks, if sufficiently slight, might get smoothed out by this process, and that the method is far more likely to cause such disappearances than to introduce a break where it does not really exist ; a consideration which explains why a particular break might be undetected in one or more of the different series of experiments dealt with by Mr. Pickering. The extent to which the process of trial and error was carried by him may be gathered from the following quotation. "Drawings on several different scales, and with several different points as origins, were made in all cases, and the labour entailed in the treatment of the results has by far exceeded that of the determinations themselves" †.

Mr. Lupton's preference for a process "which will give the same result in all hands" irresistibly suggests a comparison between a barrel-organ and a violin. The latter is undoubtedly the superior instrument, and yet it can neither be denied that in the manipulation of the violin "a strong

* "Nature of Solutions," p. 104.
† "Nature of Solutions," p. 68.

personal element is introduced," nor that "considerable care and practice are requisite before it can be safely used." Uniformity of results can be no real argument in favour of a method, which, as I have above endeavoured to show, would seem by its very nature incapable of being applied in practice so as to deal effectively with the question at issue.

Mr. Lupton attempts to clinch his argument by applying an arithmetical process to some ten or a dozen density determinations forming only a small part of one of Mr. Pickering's series of experiments. In order to exhibit the value of the method, he is, of course, compelled to take them so that they include an assumed break, but minimises this disadvantage by choosing them in a region where, according to Mr. Pickering, the curve "is of a very doubtful character." * Although under the circumstances the chances in favour of a very fair agreement between the observed and calculated values were considerable, the result is most unsatisfactory from Mr. Lupton's point of view. He seems to have been misled by a statement of Mr. Pickering as to 0·0002 gram being a safe limit of error; but, since the piknometer held 25 c.c., the corresponding error in the density is, as Mr. Pickering says, only 0·000008, which is far exceeded by *every one* of the differences between observed and calculated values tabulated by Mr. Lupton. Even if the limit of error were ten times as great as the above, it would only mend the matter in *two* cases, and this occurs in spite of the fact that his equation contains *three* arbitrary constants. Comment is needless.

There are several minor points in Mr. Lupton's paper which call for some remark. After making an assertion concerning the equation of the second degree which is untrue unless it happens to represent a parabola whose axis is parallel to the axis of y, he proceeds to say, "Hence the hydrates of sulphuric acid are apparently made to depend upon the flexibility of the steel lath used." † It is extremely difficult to fathom the precise meaning of this statement, still more so to see how it depends upon the preceding one. It may, however, be as well to point out that any two uniform laths may be bent so as to form identical curves (provided of course that the bending does not exceed a certain limit), although if the flexural rigidity (stiffness) were too great the operation might be trying to the fingers.

Mr. Lupton very rightly remarks that "the assumption

* "Nature of Solutions," p. 76.

† P. 421.

that $\phi(x)$ can be expanded in ascending powers of x is by no means universally true." * This fact tells to a certain extent in favour of methods (such as Mr. Pickering's) in which no such assumption is made.

Exception is taken to Mr. Pickering's "dealing with an abscissa of 50·06998 . . . . and a corresponding ordinate of 1·404296" †. It may be freely conceded that as regards the abscissa, the last two figures cannot affect the diagram, but it may be presumed that the actual experiments have some value apart from the present application. Mr. Lupton appears to have momentarily forgotten that Mr. Pickering's chart refers to the first differential. He will find if he looks again at the table ‡, that in the values of $\frac{ds}{dp}$ the figures in the sixth decimal place have been deliberately omitted. The figures in the fifth place would tell, even on the small scale of the published diagram.

It is a little hard too on Mr. Pickering that he should be attacked for his use of the term "differentiation," in which he is only following others, when he so carefully explains what he means by it §. He notes the distinction between differences and differentials, and even goes so far as to call attention to the fact that irregularities will be caused if the intervals are not equal. It is interesting to notice that if the curves dealt with are parabolas whose equation is of the form $y=a+bx+cx^2$, the value of $\frac{y_2-y_1}{x_2-x_1}$ (called by Mr. Pickering a differential) is actually the same as that of $\frac{dy}{dx}$ (the true differential coefficient) at the point whose abscissa is $\frac{x_1+x_2}{2}$.

Before concluding these remarks I wish to call attention to what is really the strongest, though not perhaps the most striking argument in favour of Mr. Pickering's conclusions: the general agreement of the results obtained from the study of various properties, and the apparent absence of any inexplicable discrepancy in special cases. It is strange that Mr. Lupton should not only have ignored this aspect of the question, but should even have used an expression ‖ which would seem to imply that there was an absence of confirmatory evidence derived from different sources. The importance of the omission can scarcely be overrated.

* P. 421.
† P. 420.
‡ "Nature of Solutions," p. 142.
§ *Id.* p. 67.
‖ "In the hurry of modern life" (experimentalists) "are apt to omit the test of accuracy afforded by obtaining the same results by several different methods," p. 419.

[I have been informed that a very high authority has brought forward as an argument against Mr. Pickering's methods the fact that a spring (or lath) may be pinned down so as to coincide to any desired degree of accuracy with any number of experimental points, and trust that I may be excused if I attempt to answer the objection. The use of an unlimited number of applied forces (one at each pin) is open to the same theoretical objections as would apply to an equation containing an unlimited number of constants. As Mr. Pickering used for drawing his curves a part of the lath throughout which no applied forces were acting, two distinct curves of the kind used by him would meet at each pin, and a discontinuity would exist, which can be shown by mathematical analysis to involve an abrupt change in the value of $\frac{d^3y}{dx^3}$, *i. e.* there would be a *break* at these points. Rapid changes too in the value of $\frac{d^2y}{dx^2}$ might take place if the applied forces were large, or the flexural rigidity of the lath small. In fact the pinning-down process simply masks any real breaks which may exist by substituting a (probably much larger) number of others. It would even seem to be theoretically possible that experiments as to the minimum number of applied forces required might indicate the points at which the breaks occur.—E. H. H.]

XVII. *On the Construction of Platinum Thermometers. By* H. L. Callendar, *M.A., Fellow of Trinity College, Cambridge* *.

THE great superiority of the platinum-resistance thermometer over other instruments for measuring temperature lies in its comparative freedom from change of zero. Provided that the wire is pure to start with, and that it is protected from strain and from contamination, its resistance, when once annealed, is always very nearly the same at the same temperature.

This statement, which I made in 1886, has been received in some quarters with surprise and incredulity. The evidence on which it has been rejected appears to rest mainly on two well-known facts. Firstly, that the Siemens electrical pyrometers have always shown large and continuous changes of zero†; and, secondly, that platinum wires when used as

* Communicated by the Author.

† British Association Report, 1874.

filaments for incandescent lamps undergo more or less rapid deterioration.

The Siemens pyrometer is a commercial and not a scientific instrument. I have myself examined some of the most recent pattern, and I should have been surprised if they had not been found to exhibit changes of zero when used at high temperatures. The wire is wound on common clay, which is apt to attack it, and is inclosed in an iron tube without sufficient protection from the metallic and other vapours which are sure to be present.

In the case of lamp-filaments which are heated by a current *in vacuo*, it might appear at first sight as though the wire were perfectly protected from strain or contamination; but this is far from being the case. The sudden heating and cooling of the wire when the current is turned on or off, and the intense radiation which keeps the surface at a lower temperature than the central portions, must be a severe strain on the wire. It is also evident that any crack or flaw in the surface will tend to be intensified by the local development of greater heat; and if the wire is heated to a temperature near its melting-point where it begins to be appreciably volatile, this action must inevitably produce serious results. If a wire which has been thus treated be examined under the microscope, its surface will generally be found to be cracked and scored in a manner which is of itself amply sufficient to account for the increased resistance and brittleness.

The wire of a platinum thermometer which is properly protected does not undergo any alterations of this kind, if treated with reasonable care. I have recently succeeded in making these thermometers of a very convenient and accurate form; and I have reason to believe, from inquiries which have reached me from various sources, that a description of the pattern which I have found to give the best results would be useful to other observers who require a sensitive and trustworthy thermometer.

The simplest form of platinum thermometer is made by fusing or welding a coil of fine wire to leads of relatively low resistance. The coil and leads must be suitably insulated and supported; for most purposes it is convenient to inclose the instrument in a tube of similar dimensions to an ordinary thermometer. For use at temperatures below 700° C. the leads may be of copper or silver, and the tube of hard glass.

For rough work at temperatures below 1000° C. very fair results may be obtained by the use of a wrought-iron tube. The leads should also be made of iron. Copper and silver are too volatile. Their vapours will attack the platinum, and

very small traces of either are sufficient to ruin the wire for thermometric purposes.

For accurate work at high temperatures it is necessary to use platinum leads, and to inclose the coil in a tube of glazed porcelain or silica.

For insulating the coil and leads I have found nothing that answers so well as mica. Biscuit porcelain is fairly good, but most varieties of clay are apt to attack the wire at high temperatures. If the wire is wound on a clay cylinder, the relatively large mass of the clay has also the effect of materially reducing the sensitiveness.

The wire is preferably doubled on itself like an ordinary resistance-coil, and wound on a thin plate of mica. The leads are insulated by being made to pass through a series of mica wads cut to fit the tube containing the instrument. This method has the advantage of giving very perfect insulation, and of preventing convection-currents of air up and down the tube.

The resistance of such an instrument may conveniently be measured by means of an ordinary post-office box. If the resistance-coils are of German-silver wire, the temperature of the box must be taken at each observation and a correction applied. It is better therefore to use a box with coils of copper-nickel-manganese, or one of the many other alloys that do not change appreciably in resistance at ordinary temperatures.

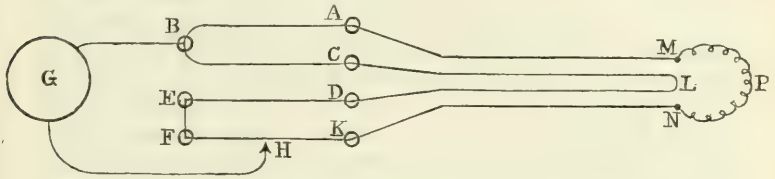
With the above simple arrangement it is not difficult to obtain results consistent to a few hundredths of a degree at 500° C., provided that the resistance of the leads is relatively very small and fairly constant, and that the stem of the thermometer is always immersed to nearly the same extent. There are some objections, however, to the use of thick leads. They are necessarily wanting in lightness and flexibility, and they tend to cool the bulb of the thermometer by conduction along the stem.

For most purposes it is better to insert in the stem of the thermometer a second pair of leads similar to those of the coil itself, so that their resistance can be measured separately. It is then possible to use leads of any convenient length and flexibility, and to make the observations of temperature independent of the length of stem immersed.

In the ordinary method of measuring a resistance with a post-office box, it is necessary to observe galvanometer-throws in order to find the last two figures of the value of the resistance. If, however, a divided bridge-wire be used in conjunction with the resistance-box for determining the frac-

tions of an ohm in the manner now to be described, the apparatus can at the same time be arranged so that the variable resistance of the leads is eliminated. The reading of the bridge-wire scale when the balance is found is then independent of the length of stem immersed, and gives the temperature of the thermometer-coil without the necessity of observing galvanometer-throws or of measuring the resistance of the leads.

The annexed figure represents, somewhat diagrammatically, the arrangement of the apparatus.



A B, B C are equal resistances forming the arms of the balance. The battery is connected at A and C, and one terminal of the galvanometer G at B. D E represents a set of resistance-coils, which together with A B and B C may be supplied by an ordinary post-office box. F K represents a straight bridge-wire with a divided scale attached. The other terminal of the galvanometer is connected to the contact-piece H, which slides along this wire. The leads A M, K N, from the pyrometer-coil P, are connected to A and K; and the compensating leads C L, L D, the resistance of which is equal to A M, K N, are connected to C and D. These four leads may be of any convenient length; they are symmetrically arranged so that corresponding parts are always at the same temperature. When the balance is found by unplugging suitable resistances in the arm D E and sliding the contact-piece H, it is plain that, since the resistances A B, B C are equal, the resistance of the pyrometer and its leads, plus that of the length H K of the bridge-wire, will be equal to the resistance of the remaining portion F H of the bridge-wire together with that of the coils D E and the compensator C L D. Thus the changes of resistance of the pyrometer-leads A M, K N are compensated by the equal changes in the leads C L, L D; and the resistance of the pyrometer-coil itself is directly given by the sum of the coils D E and the reading of the bridge-wire.

It is convenient to graduate the bridge-wire scale so that 100 or 1000 divisions are equivalent to the unit coil in the arm D E. It is also convenient to adjust the resistance of the

pyrometer-coil, so that the change of its resistance between 0° and 100° C. may be equal to 1, 10, or 100 units. The divisions of the bridge-wire will then represent degrees of temperature on the platinum scale, and the temperature can be deduced from the observed resistance by simply subtracting its zero value.

The arrangement, however, will work equally well with an arbitrary scale. The really important point is that an observation of temperature is reduced to a single scale-reading, and that it is independent of the length of stem immersed.

The chief errors to be apprehended with this form of apparatus are changes in the screw and plug contacts, especially the latter. Instead of the ordinary plug for short-circuiting the terminals of a resistance-coil, I prefer to use a flat nut screwing down on to two flat plates. I find that better contact may thus be secured, and, what is more important, that the contact-surfaces may be more easily kept clean and good. It is almost impossible to keep a plug-hole free from grit and grease, even if the plug fits perfectly; whereas the screw-nut can be kept screwed down when not in use, and the flat surfaces are easily cleaned if necessary. Moreover the wedge-like action of the plugs almost invariably loosens the blocks between which they are inserted, so that taking out one plug alters the contacts of its neighbours. This cannot occur with the screw-nuts. Among minor advantages it may be mentioned that the screw-nuts, not being loose, are not so liable to get lost or soiled.

Perhaps the best way to make the sliding-contact at H is to connect the galvanometer to a fixed wire of the same material as F K and stretched parallel to it. Connexion is made between the two wires by pressing down a button carrying a short cross-wire fixed to a spring on the lower side of the sliding contact-piece. The advantages of this arrangement are that the wire from the galvanometer is not attached to the sliding-piece itself but to a *fixed* binding-screw, and that there is less danger of thermoelectric effects being produced by the warmth of the hand at H.

The current used in measuring the resistance must not be too large or the fine wire will be heated. It appears that a platinum wire of 0·015 centim. (·006 inch) diam., which is a convenient size to use for these thermometers, will take a current of one hundredth of an ampere when cooled by air contact, without heating much more than one hundredth of a degree C. If a higher order of accuracy is desired, the current-heating must be measured and allowed for.

The degree of sensitiveness and accuracy attainable with

these instruments depends largely on the adjustment of the galvanometer and on the perfection of the optical means for reading its deflexions. A convenient method is to use a microscope * with a micrometer-eyepiece, and to observe the reflected image in the galvanometer-mirror of a scale attached to the objective. The power of the microscope in magnifying the deflexions is proportional to the length of its body and to the power of the eyepiece, and does not depend on the focal length of the objective. A telescope does equally well, but the arrangement is then less compact. Either method is superior to the lamp and scale in point of accuracy and for other reasons, particularly in not requiring a darkened room. This is a great advantage, because a good light is preferable for reading the scale of the bridge-wire and noting down the observations.

With regard to the formula to be used for reducing the observed platinum-temperature pt to the temperature t by air-thermometer, the very careful experiments made by Griffiths on the boiling- and freezing-points of various substances † seem to show that the simple parabolic formula

$$t-pt=\delta\{t/100)^2-t/100\} \quad . \quad . \quad . \quad . \quad . \quad (d)$$

holds over a wide range even more accurately than I had previously imagined. The values of t for various boiling- and freezing-points, deduced by the aid of this formula from observations with thermometers of very different patterns and with different coefficients, were rarely found to differ from each other by more than a few hundredths of a degree over the range 0°–450° C. The value of the constant δ for any thermometer may be readily deduced from a single observation of the boiling-point of sulphur or mercury as described in the paper above referred to ‡.

The air-thermometer experiments § on which this formula was founded did not extend beyond 650° C., but I have recently succeeded in verifying it roughly at a higher temperature by an observation of the freezing-point of silver. This point appears to be very clearly marked and well adapted for a high-temperature standard. Several independent observations with a platinum thermometer gave the same result, 982°·1 C., within a small fraction of a degree. The specimen of silver, however, was not perfectly pure, so that the result

* I owe this suggestion to Mr. Horace Darwin of the Instrument Co., Cambridge, to whom I am also much indebted for the care and skill bestowed on the construction of my apparatus.

† Phil. Trans. 1891, A. pp. 43 & 148.

‡ Phil. Trans. 1891, A. p. 146. § Phil. Trans. 1887, A. p. 161.

is probably a little too low. Moreover, on account of the wide discrepancies at present existing in the estimates of the temperature of the freezing-point of silver on the air-thermometer scale, according to different authorities, the result would in any case serve only as a *rough* verification of the formula (*d*). The difficulties in the way of making accurate determinations with an air-thermometer at this temperature are undoubtedly considerable; but I have recently succeeded in devising a special form of instrument with which I hope to be able to obtain more trustworthy results.

Sir Wm. Siemens was the first to attack the problem of determining the variation of electrical resistance at high temperatures. He showed that the formula given by Matthiessen,

$$R_0/R_t = 1 - \alpha t + \beta t^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (m)$$

was entirely inapplicable except between the limits 0° and 100° C. His own experiments led him to suggest the formula

$$R = \alpha T^{\frac{1}{2}} + \beta T + \gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (S)$$

This formula has been very widely quoted and adopted, but it does not, so far as my experience goes, represent the results of observation so well as the simpler formula $R/R_0 = 1 + \alpha t + \beta t^2$, which was used by Benoit, and which is equivalent to formula (*d*).

I have only recently succeeded in finding a published account of Sir Wm. Siemens's experiments *. It appears from this that they were undertaken rather with a view of graduating a commercial pyrometer than of investigating the law of change of electrical resistance. Temperatures up to 350° were determined *by mercury thermometers* in an air- or oil-bath, and it does not appear that any corrections were applied to their readings. The individual observations are somewhat irregular, and often show divergencies amounting to 2 per cent. and over. Only three observations at higher temperatures are given; they show a mean deviation of about 30° C. A copper ball-pyrometer was used to determine the temperatures, which are given as 810°, 835°, and 854° C.; the corresponding temperatures deduced by formula (S) from the observed resistances of the platinum pyrometer were 772°, 811°, and 882° C.

The formula Siemens gives for *iron* makes the rate of increase of its resistance *diminish* considerably with rise of temperature. The formula given by Benoit makes it *increase*

* 'Transactions of the Society of Telegraph Engineers,' 1875.

very largely. All the specimens I have tried agree very closely with Benoit's formula. I am inclined to think that the Siemens formula must be wrong. It is at least noteworthy that two of his observations differ by 6 and $3\frac{1}{2}$ per cent. respectively from his formula in the direction of agreeing with Benoit's, and that if allowance is made for the probable errors of the mercury thermometers at 350° the discrepancy may be still further reduced. The resistances apparently were only measured to about 1 per cent. in most cases, and the temperatures are given only to the nearest degree. The Siemens formula is undoubtedly superior to that given by Matthiessen, but the evidence in its favour is hardly sufficient to justify its continued use in preference to the much simpler and more convenient formula (*d*).

The superior capabilities of platinum thermometers as compared with instruments in general use do not appear as yet to be sufficiently appreciated. It will perhaps help to bring out more clearly several of the points mentioned in their construction, if I give a brief summary of some of the advantages which they present in point of range, constancy, and sensitiveness, as compared with the best mercury thermometers.

The range of a mercury thermometer is obviously limited to temperatures between −40° and +400° C. That of a platinum thermometer may extend from absolute zero to above 1500° C.

The superiority of the platinum thermometer is still greater in point of constancy. It is a fact familiar to those who have studied mercury thermometers, that if a new thermometer be kept at a temperature of 350° C. for a week or so, its zero will be found to rise by 10° or 20° owing to the contraction of the glass. After a time this rise reaches a limit ; but if a thermometer which has been thus annealed and allowed to cool *slowly* be again heated to 350° for a few minutes and allowed to cool *rapidly* by free exposure to the air, its zero will be found to be *depressed* by a quantity which varies with different thermometers, but which generally amounts to about 2°. A similar depression, but less in amount, is observed if the thermometer is heated to some intermediate point of the scale. The extent of depression also depends on the time during which the thermometer is heated, and on the rate at which it is cooled. Thus even in the best mercury thermometers, which have been carefully annealed by a special process, the position of the zero is constantly shifting in a manner which depends on the past history of the instrument. It is consequently very difficult, and in many cases

impossible, to attain an accuracy of the order of a tenth of a degree even at temperatures as low as 200° C.

On the other hand, when a platinum thermometer has once been annealed (a process which can be completed in a few minutes), its zero will not be found to vary even by a hundredth of a degree—if it is properly constructed—when used at any temperatures up to 500° C.; and in some thermometers which I have used at temperatures as high as 1300° C., I have not found any changes of zero amounting to more than a tenth of a degree.

Sensitiveness and rapidity of observation are often of considerable importance. A mercury thermometer with an open scale must necessarily contain a relatively large mass of mercury, since there are objections to unduly diminishing the bore of the tube. Thus it cannot be made so sensitive as a platinum thermometer in which the actual mass of metal may be very small. A still more important point is that, owing to the imperfect elasticity of the glass, it is desirable to allow the mercury thermometer some time to settle before taking a reading. This is of course unnecessary in the case of the platinum thermometer.

In ordinary work with mercury thermometers it is generally necessary to expose some portion of the stem to the air. If a volume of mercury corresponding to any considerable number of degrees be thus exposed, the error becomes serious. It may amount to as much as 10° at 350° C. This correction is so uncertain that it is now generally considered inexpedient to attempt to apply it. The only way to avoid it, and at the same time to secure a sufficiently open scale for accurate work without unduly increasing the length of the stem, is to use a *series* of thermometers of "limited scale." Each of these must have at least two points of its scale specially determined. It has hitherto been the custom to graduate such thermometers by means of substances of known boiling- and freezing-points; but, as Griffiths * has shown, the graduation may be much more easily and accurately effected by comparison with a single platinum thermometer, a method which has the further advantage of saving the trouble of calibrating the stem.

It is easy to construct a platinum thermometer with a scale of 1 centim., or even 10 centim., to the degree, whose reading shall be entirely independent of the length of stem immersed. The divided wire on which the readings are taken need not be more than 20 centim. in length, and can be made to correspond to any part of the scale by simply unplugging a few

* B. A. Report, 1890.

resistances. Thus a single platinum thermometer will do the work of a whole series of mercury thermometers, and that with far greater accuracy and without the necessity of applying any troublesome and uncertain corrections.

It may be objected that the use of a platinum thermometer requires electrical apparatus and some knowledge of electrical measurement. I quite admit that it requires some special skill and experience to *make* a good thermometer, but the rest of the apparatus required is obtainable in almost any laboratory, and it is easy to take the readings quickly and accurately after a little practice. The great superiority of the platinum thermometer in range, accuracy, and durability, will be found in the end to save so much time and expense as will more than compensate for the small trouble of learning to use it.

XVIII. *On a probable Relationship between Specific Inductive Capacity and Latent Heat of Vaporization.* *By* Eugene Obach, *Ph.D., F.C.S.**

THE discovery of a near relationship between physical constants hitherto considered independent of each other seems of sufficient interest to merit a place in the Philosophical Magazine, notwithstanding that the experimental data which can be brought forward in support of such relationship are somewhat meagre and not particularly accurate.

I have recently been led to investigate whether specific inductive capacity and latent heat of vaporization of a liquid are in any way related to each other, and I find this actually to be the case, at least as far as certain series of chemically related organic compounds are concerned, viz. the esters of formic, acetic, and benzoic acid, and the monatomic alcohols. For these bodies, as will be shown hereafter, inductive capacity and latent heat are directly proportional.

The numerical values of these two physical constants obtained by different observers are in many cases very discordant; and it was therefore considered desirable to adhere as far as possible to the figures given by one and the same authority, and to introduce those of others only where absolutely necessary.

The specific inductive capacities here adopted are those published by S. Tereschin† in 1889, and the latent heats of

* Communicated by the Author.

† Wied. *Annal.* vol. xxxvi. pp. 792–804 (1889).

vaporization those found by R. Schiff* in 1886. The latent heats of the alcohols and acids are those obtained by Favre and Silbermann†, whereas for methyl formate‡, propylic alcohol, and the benzoic esters they had to be calculated by Trouton's§ relation from the molecular weight and the absolute boiling-temperature. This relation can be expressed by the formula $\lambda' = C\frac{T}{M}$, where λ' is the latent heat of vaporization, T the absolute boiling-temperature ‖, M the molecular weight, and C a constant; and since it has been entirely confirmed by Schiff's subsequent researches, it can confidently be applied to the calculation of the latent heat of most bodies, especially that of intermediate members of a series of chemically related compounds. The average value of the constant C, found by Schiff, is 20·8; but for the alcohol series I adopted the figure 25·86, deduced from Favre and Silbermann's determination of the latent heat of water, which gave practically the same result as that found by Regnault, Andrews, and Berthelot. This constant is not very different to that deduced directly from the alcohols, viz. 26·14.

In the following Tables I. and IV. the calculated values of the latent heats are enclosed in brackets in order to distinguish them from those actually found by experiment.

Table I. gives the latent heat of vaporization λ, the specific inductive capacity K, and the quotient $\frac{\lambda}{K}$ for the principal esters of formic acid. Table II. similarly gives these values for the esters of acetic acid, and Table III. for the ethyl esters of the principal monobasic fatty acids; the esters of formic acid being represented by the general formula $H.CO_2(C_nH_{2n+1})$, those of acetic acid by $CH_3.CO_2(C_nH_{2n+1})$, and the ethylic esters of the fatty acids by $(C_nH_{2n-1}O)OC_2H_5$. Since no experimental data for the latent heat of the benzoic-acid esters $C_6H_5.CO_2(C_nH_{2n+1})$ are available, this series of compounds will be referred to later on (*vide* Table V.).

Table IV. gives the experimental results for the saturated monatomic alcohols $(C_nH_{2n+1})OH$. In Tables I., II., and IV.

* Liebig's *Annal.* vol. ccxxxiv. pp. 338–350 (1886); also *Beiblätter* zu Wied. *Annal.* vol. x. pp. 689–692 (1886).

† Landolt Börnstein's Tables, pp. 189–190 (1883).

‡ The values given for methyl formate by Andrews and Berthelot seem too high.

§ Phil. Mag. [5] xviii. pp. 54–57 (1884).

‖ The boiling-temperatures are mostly taken from the latest edition of Beilstein's *Handbuch der organischen Chemie*, and nearly all refer to the normal pressure of 760 millim.

the complete series are given from $n=0$ to $n=5$, the first members being formic acid, acetic acid, and water respectively, and the last the amyl compounds*. For the acids the specific inductive capacity is not known, but I have calculated it from the mean ratio $\frac{\lambda}{K}$ of each particular series. If these calculated values of K should in future be compared with those found by direct observation, it must be borne in mind that the values found by Favre and Silbermann for the latent heat of these acids are probably not quite accurate. For the specific inductive capacity of water, E. B. Rosa's† value, viz. 75·7, is adopted, Tereschin's figure, 83·8, being notably higher; whilst the results obtained by the same observers for ethylic alcohol are almost identical, viz. 25·7 and 25·8 respectively.

It will be seen from Tables I., II., and IV. that the deviations of the individual values of the quotient $\frac{\lambda}{K}$ from the mean are no greater than one would expect, considering that the two constants were obtained by different observers and with entirely different samples of liquid. In the case of the acetates and alcohols, which form two almost complete series, the constancy of the quotient $\frac{\lambda}{K}$ is particularly satisfactory; and when the observed values are plotted out, taking the latent heats as abscissæ and the inductive capacities as ordinates (*vide* the diagram), the points of intersection are nearly equally distributed on both sides of a straight line, thus unmistakably showing the linear dependency of the two physical constants. Returning to Table III., which embodies the results for five different ethyl esters, it will be noticed that the ratio $\frac{\lambda}{K}$ is not quite so constant, but rather seems to increase with the molecular weight; however, if the first member of this group, viz. ethyl formate, is disregarded, the deviations from the mean are by no means very great.

In order to show the legitimacy of employing calculated values of latent heat, where no direct determinations are available, *e.g.* for the benzoic-acid esters, I have also calculated them for those bodies where experimental values actually do

* Schiff's determinations of the latent heat refer to the isoamyl esters, but it is doubtful if this is also the case with Tereschin's specific inductive capacities. The normal amyl formate is not mentioned in Beilstein's Handbook.

† Phil. Mag. [5] xxxi. p. 200 (1891).

exist, viz. for the various esters of fatty acids and for the alcohols.

Tables I. *a*, II. *a*, III. *a*, and IV. *a* contain the results of these calculations, they show that the constancy of the quotient $\frac{\lambda'}{K}$ is quite as good as in the corresponding tables containing the observed values of λ. We are, therefore, justified in regarding the results obtained for the benzoic-acid esters given in Table V. with the same degree of confidence as those of the other series, and to conclude that these compounds also show the direct relationship between inductive capacity and latent heat. This is the more interesting, as the benzoic esters belong to the entirely distinct class of aromatic compounds.

It will be observed from Tables I. *a* and II. *a* that the latent heats of the free acids, calculated with Schiff's constant 20·8, differ widely from those actually found, and in order to obtain a better agreement the constant would have to be reduced to 15·1; but if in place of the boiling-temperatures actually observed, those which would follow from the position of the acid in the particular ester series were employed, viz. 283° for formic and 311° for acetic acid, the resulting latent heats of vaporization would become 128 and 108 respectively *, which is in better accordance with the experimental results, and gives for K the more probable values 13·1 and 8·8. However, the higher members of the series, viz. butyric and valeric acid, also examined by Favre and Silbermann, do not conform to this rule. Table VI. gives, for direct comparison, the mean values of the ratios $\frac{\lambda}{K}$ and $\frac{\lambda'}{K}$ for all five series hitherto considered, and it will be seen that there is practically very little difference between them. There is also only little difference between the mean ratios of the formic and benzoic esters, and, again, between those of the acetic esters and the esters of the higher acids, whereas the alcohols give a notably lower ratio.

* Trouton (*l.c.* p. 5) increases the theoretical vapour-density of formic acid in the ratio 2·68 : 1·62, and that of acetic acid in the ratio 3·19 : 2·08, for the calculation of his constant. If the molecular weights are similarly increased, the latent heats, calculated from the actual boiling-temperatures with Schiff's mean constant, are about 20 per cent. below the observed values; but if the constant derived from water, which I applied to the alcohol series, is taken, the results are practically the same as those given above, viz. 127 and 110 respectively.

TABLE I.

Formic-Acid Esters, H . $CO_2(C_nH_{2n+1})$.

Carbon atoms in Alcohol radical (n)	0 (Acid.)	1	2	3	4	5
Name of Radical	(Hydrogen)	Methyl.	Ethyl.	Propyl.	Isobutyl.	Amyl.
Latent heat of vapor. (λ)	120·7*	(105·8)	92·2	85·2	77·0	Iso. 71·7
Spec. Induct. Capacity (K)	[12·3]	9·9	9·1	[8·7]	8·4	7·7
Ratio $\frac{\lambda}{K}$	—	10·7	10·1	—	9·2	9·3
		Mean = 9·83 ± 0·35.				

* Favre and Silbermann.

TABLE I. *a*.

Formic-Acid Esters, H . $CO_2(C_nH_{2n+1})$.

Carbon atoms in Alcohol radical (n)	0 (Acid.)	1	2	3	4	5
Name of Radical	(Hydrogen)	Methyl.	Ethyl.	Propyl.	Isobutyl.	Amyl.
Absol. boiling-temp. (T)	374	305	327	354	371	Iso. 396
Molecular weight (M)	46	60	74	88	102	116
Calcul. latent heat of vaporization (λ')	(169·1)*	105·8	91·9	83·7	75·7	71·0
Spec. Induct. Capacity (K)	—	9·9	9·1	[8·6]	8·4	7·7
Ratio $\frac{\lambda'}{K}$	—	10·7	10·1	—	9·0	9·2
		Mean = 9·75 ± 0·40.				

* This would give [17·3] for K, which is undoubtedly too high.

TABLE II.

Acetic-Acid Esters, $CH_3 . CO_2(C_nH_{2n+1})$.

Carbon atoms in Alcohol radical (n)	0 (Acid.)	1	2	3	4	5
Name of Radical	(Hydrogen)	Methyl.	Ethyl.	Propyl.	Isobutyl.	Amyl.
Latent heat of vapor. (λ)	101·9*	94·0	83·0	77·3	69·9	Iso. 66·3
Spec. Induct. Capacity (K)	[8·2]	7·8	6·5	6·3	5·8	5·2
Ratio $\frac{\lambda}{K}$	—	12·0	12·8	12·3	12·1	12·8
		Mean = 12·40 ± 0·17.				

* Favre and Silbermann.

TABLE II. *a*.

Acetic-Acid Esters, $CH_3 . CO_2(C_nH_{2n+1})$.

Carbon atoms in Alcohol radical (n)	0 (Acid.)	1	2	3	4	5
Name of Radical	(Hydrogen)	Methyl.	Ethyl.	Propyl.	Isobutyl.	Amyl.
Absol. boiling-temp. (T)	395	330	350	374	389	Iso. 412
Molecular weight (M)	60	74	88	102	116	130
Calcul. latent heat of vaporization... (λ')	(136·9)*	92·8	82·7	76·3	69·8	65·9
Spec. Induct. Capac. (K)	—	7·8	6·5	6·3	5·8	5·2
Ratio $\frac{\lambda'}{K}$	—	11·9	12·7	12·1	12·0	12·7
		Mean = 12·28 ± 0·17.				

* This would give [11·1] for K, which seems also too high.

TABLE III.

Ethyl Esters, $(C_nH_{2n-1}O)OC_2H_5$.

Carbon atoms in Acid radical (n)	1	2	3	4	5
Name of Radical	Formyl.	Acetyl.	Propionyl.	Butyryl.	Valeryl.
Latent heat of vapor. (λ)	92·2	83·0	77·1	71·5	64·6
Spec. Induct. Capac. (K)	9·1	6·5	6·0	5·3	4·9
Ratio $\frac{\lambda}{K}$	10·1	12·8	12·8	13·5	13·2
	Mean $= 12{\cdot}48 \pm 0{\cdot}61$.				

TABLE III. *a*.

Ethyl Esters, $(C_nH_{2n-1}O)OC_2H_5$.

Carbon atoms in Acid radical (n)	1	2	3	4	5
Name of Radical	Formyl.	Acetyl.	Propionyl.	Butyryl.	Valeryl.
Absol. boiling-temp. (T)	327	350	372	392	407
Molecular weight (M)	74	88	102	116	130
Calcul. latent heat of vaporization... (λ')	91·9	82·7	75·9	70·3	65·1
Spec. Induct. Capacity (K)	9·1	6·5	6·0	5·3	4·9
Ratio $\frac{\lambda'}{K}$	10·1	12·7	12·7	13·3	13·3
	Mean $= 12{\cdot}42 \pm 0{\cdot}60$.				

TABLE IV.

Alcohols, $(C_nH_{2n+1})OH$.

Carbon atoms in Alcohol radical (n)	0 (Water.)	1	2	3	4	5
Name of Radical	(Hydrogen)	Methyl.	Ethyl.	Propyl.	Butyl.	Amyl.
Latent heat of vapor. (λ) ...	535·8*	263·9*	208·9*	(159·5)	(135·2)	121·4*
Spec. Induct. Capacity (K)...	75·7†	32·7	25·8	22·8	[17·9]	15·9
Ratio $\frac{\lambda}{K}$	7·1	8·1	8·1	7·0	—	7·6
		Mean = 7·58 ± 0·24				

* Favre and Silbermann. † E. B. Rosa.

TABLE IV. *a*.

Alcohols, $(C_nH_{2n+1})OH$.

Carbon atoms in Alcohol radical (n)	0 (Water.)	1	2	3	4	5
Name of Radical	(Hydrogen)	Methyl.	Ethyl.	Propyl.	Butyl.	Amyl.
Absol. boiling-temp. (T)	373	339	351	370	387	410
Molecular weight (M)	18	32	46	60	74	88
Calcul. latent heat of vaporization ... (λ') ...	535·8	273·9	197·3	159·5	135·2	120·5
Spec. Induct. Capacity (K)...	75·7	32·7	25·8	22·8	[17·9]	15·9
Ratio $\frac{\lambda'}{K}$	7·1	8·4	7·7	7·0	—	7·6
		Mean = 7·56 ± 0·32.				

TABLE V.

Benzoic-Acid Esters, $C_6H_5 . CO_2(C_nH_{2n+1})$.

Carbon atoms in Alcohol radical (n)	1	2	3	4	5
Name of Radical	Methyl.	Ethyl.	Propyl.	Isobutyl.	Isoamyl.
Absol. boiling-temp. (T)	468	484	503	510	535
Molecular weight (M)	136	150	164	178	192
Calcul. latent heat of vaporization (λ').	71·6	67·1	63·8	59·6	58·0
Spec. Induct. Capacity (K)	7·2	6·5	[6·2]	6·0	5·2
Ratio $\frac{\lambda'}{K}$	9·9	10·3	—	9·9	11·2
	Mean = 10·33 ± 0·31.				

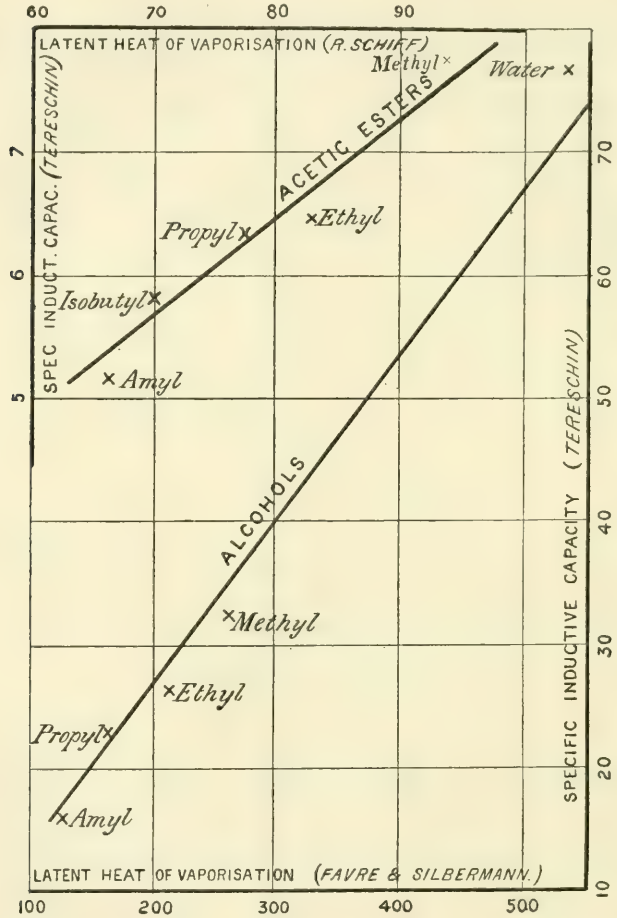
TABLE VI.

Summary of the mean ratios $\frac{\lambda}{K}$ and $\frac{\lambda'}{K}$.

(From preceding Tables.)

Description of Series	Formic Esters.	Acetic Esters.	Ethyl Esters.	Monatomic Alcohols.	Benzoic Esters.
Vide Tables	I. & I. *a*.	II. & II. *a*.	III. & III. *a*.	IV. & IV. *a*.	V.
Observed Latent Heat	9·83	12·40	12·48	7·58	—
Calculated Latent Heat	9·75	12·28	12·42	7·56	10·33

If for a series of chemically related bodies $\frac{\lambda'}{K}=\gamma$, or $\lambda'=\gamma K$, it follows from Trouton's relation that $\gamma K = C\frac{T}{M}$, or $KM=C'T$, when $C'=\frac{C}{\gamma}$, i. e. *the absolute boiling-temperature*



of any member of a series is proportional to the product of molecular weight and specific inductive capacity, or, in other words, to the *molecular inductive capacity*. The numerical value of the constant C′ for any given series of compounds

depends solely upon the units chosen. For instance, when the latent heat is based, as usual, on the specific heat of water, the gramme weight, and the Centigrade scale, and when the inductive capacity is compared with that of air taken as unity, the ratio $C' = \frac{C}{\gamma}$ becomes *e. g.* for the acetic-acid series $\frac{20{\cdot}8}{12{\cdot}28} = 1{\cdot}694$.

In place of the molecular weights, Trouton originally used the vapour-densities D based on H_2 as unity ; the value of his constant consequently lies between 10 and 13. It will be noticed that these figures are not very different to the constant γ obtained for the various ester series. In those cases where the two happen to be identical, the relation between specific inductive capacity, vapour-density, and absolute boiling-temperature, can be expressed by the extremely simple formula KD = T.

De Heen has shown* that the absolute boiling-temperature T at 760 millim. pressure and the coefficient of expansion α_0 at 0° are inversely proportional, or $\alpha_0 T = \text{constant}$; it therefore follows that $\alpha_0 KM = \text{constant}$, i. e. *the coefficient of expansion at 0° is inversely proportional to the molecular inductive capacity.* The product $\alpha_0 KM$ is perfectly analogous to the first term $\alpha_0 \rho_0 M$ in de Heen's equation for intramolecular work, which represents that part of the heat spent for physical dissociation as contradistinguished from chemical dissociation forming the second term, and to which electrolytical decomposition would here correspond.

Tereschin has already tried if there is any direct connexion between the specific inductive capacity of the various bodies which he examined and their molecular weight, and found that the two formulæ $K = a + b\frac{\sigma}{M}$ and $K = n^2\left(1 + A\frac{\sigma}{M}\right)$, where a, b, and A are constants, σ the specific gravity, and n the refractive index, fairly represent his observations. These formulæ are more complicated than the one which I have proposed, viz. $K = C'\frac{T}{M}$, without affording a notably better agreement with the experimental results, as will be seen on comparing Tereschin's calculated values given in the *Annalen* with those in the following Table VII. :—

* *Vide* abstract of Schiff's article in the *Beiblätter*, l. c. p. 691.

TABLE VII.

Comparison of Specific Inductive Capacities calculated by the formula $K = C'\frac{T}{M}$ with those observed by Tereschin.

Description of Series.		Alcohol radical.				
		Methyl.	Ethyl.	Propyl.	Isobutyl.	Amyl.
Formates	Calculated.....	10·8	9·4	8·6	7·8	Iso. 7·3
	Observed	9·9	9·1	—	8·4	7·7
Acetates	Calculated.....	7·6	6·7	6·2	5·7	Iso. 5·3
	Observed	7·8	6·5	6·3	5·8	5·2
Benzoates	Calculated.....	6·9	6·5	6·2	5·8	Iso. 5·6
	Observed	7·2	6·5	—	6·0	5·2
Alcohols	Calculated.....	36·2	26·1	21·1	17·9	15·9
	Observed	32·7	25·8	22·8	—	15·9

The series of chemical compounds so far considered are all characterized by the fact that the alcohol radicals are indirectly linked to the carbon through the interposition of an oxygen atom; but if the radicals are directly bound to the carbon, which, for instance, is the case with the benzene hydrocarbons, proportionality between specific inductive capacity and latent heat of vaporization no longer holds good. This is evident on comparing the latent heats of these hydrocarbons found by Schiff with the inductive capacities obtained by Negreano *, where, with increasing molecular weight of the series, the former diminish and the latter slowly rise.

Besides the compounds which have already been mentioned only a few more remain, for which fairly reliable values of both specific induction and latent heat exist: these are ethylic ether, carbon tetrachloride, carbon disulphide, and oil of turpentine; but even for these bodies the inductive capacities are by no means certain, as the results obtained by different investigators and different methods show considerable variations. Carbon tetrachloride has been examined by Tereschin,

* *Comptes Rendus*, vol. civ. pp. 423–425 (1887).

and the three other compounds by G. Quincke*. I consider the latter's values obtained by the balance-method to be the most suitable for comparison with Tereschin's figures. The results are given in the following Table :—

TABLE VIII.

Various Liquids.

Name and Formula of Liquid	Ethylic Ether. $C_2H_5O.C_2H_5$.	Carbon tetrachloride. CCl_4.	Carbon disulphide. CS_2.	Oil of Turpentine. $C_{10}H_{16}$.
Latent heat of vapor. (λ) ...	89·9*	46·2*	84·8*	68·7†
Spec. Induc. Capacity (K) ...	4·32	2·20	2·57	2·21
Ratio $\frac{\lambda}{K}$	20·8	21·0	33·0	31·1
	Mean=20·90.		Mean=32·05.	

* Regnault. † Favre and Silbermann.

It will be seen from the above table that the quotient $\frac{\lambda}{K}$ is totally different to that obtained previously, but it is not impossible that the four bodies may belong to two distinct groups as indicated in the table ; however, before trustworthy conclusions in this and other directions can be drawn, considerably more experimental data would be required.

There is no doubt that a better agreement between the two constants could be obtained if the same samples of liquid were used for both determinations on account of the almost unavoidable presence of foreign bodies, especially of water, which in this case would affect both measurements in the same direction. More uniform results might also be expected if the specific induction and latent heat, which are known to vary with the temperature, were determined at the same or corresponding temperatures.

If the present communication should in any way tend to induce others to take up this interesting subject and pursue it in a systematic and exhaustive manner, my object will have been accomplished.

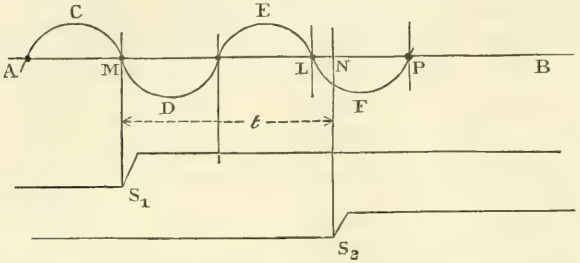
Woolwich, June 3rd, 1891.

* Wied. *Annal.* vol. xix. pp. 705–729 (1883); and *l. c.* vol. xxviii. pp. 529–538 (1886).

XIX. *An Instrument for Measuring Chronograph Traces.* *By* FREDERICK J. SMITH, *M.A., Millard Lecturer, Mech. et Phys., Trinity College, Oxford* *.

WHEN a tuning-fork is used to determine the period of time between two chronograph markings, traces such as A B, S_1, S_2 (fig. 1) are produced on a sheet of smoked

Fig. 1.

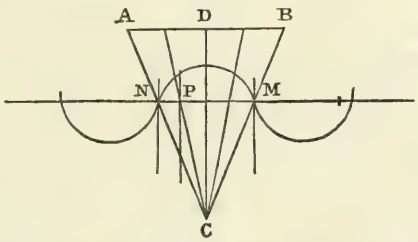


glass, which is carried in contact with the points of electromagnetic styli and the stylus of a tuning-fork. In the figure, S_1 S_2 are the markings of the electromagnetic styli, they show the beginning and ending of a time period: parallel lines ruled through S_1 S_2 cut the fork trace at M, N. The central line A B is ruled through the curved trace C D E F by the stylus of the fork when at rest, in its position of equilibrium. Hitherto I have measured a length such as *t*, which is made up of one whole vibration M L and a fraction of a vibration L N, by means of a traversing micrometer-microscope, furnished with a spider's web, or a quartz fibre, in the eye-piece. This method of determining the length of L N in terms of a vibration-length, though very accurate, has the disadvantage of taking a considerable time to go through. By means of a device which I have called the Wedge-Divider, this value may be accurately and quickly determined. A triangle (fig. 2) of which the sides A C, B C are equal is ruled on a piece of plate-glass; the base A B is divided into any number of equal parts, and each division is joined to C by straight lines. I usually divide A B into 100 parts, and each tenth line is dotted as well as ruled. To use the wedge-divider, the trace is removed from the chronograph, and after being ruled, is varnished with very thin photographic varnish. The divider is then placed upon the trace with its ruled side in contact with the trace, and moved at right angles to the trace till A C and B C cut the trace in N and M, the ends of a vibration

* Communicated by the Author.

or a half vibration-length. Thus by similar triangles the length M N is divided into the same number of equal parts as A B. This being the case, any length such as N P can be at once compared with a length N M, and consequently the time value of the length NP. I find that for accuracy, the method compares very favourably with the micrometer method, while the advantage in time of working is as about four to one. When a large number of determinations have to be reduced the question of time is important. If a well-made aluminium stylus draws a

Fig. 2.



trace on a smoked-glass surface, the trace when examined by a microscope appears to have a bright line situated midway in the cutting excavated by the stylus, this line is always used to measure from ; the edge of the trace is of no value, as its outline is usually rather like the teeth of a mason's saw. For many determinations, such as those of wave-motions in solids, it has been found convenient to use a fork having a period of $\frac{1}{500}$ second ; by using the wedge-divider, the $\frac{1}{50,000}$ second may be at once read. The surface velocity of the glass is arranged so that each vibration is about 0·8 centim. long. My first experiment, which led up to the wedge-divider used in conjunction with a microscope, was to put a trace into a projection lantern, and measure the image on a cardboard screen carrying a triangle, divided as I have described. By using the wedge-divider in close contact with the trace, in the field of a microscope, the distorsion inherent in the lantern method is eliminated.

Oxford, June 12, 1891.

XX. *Notices respecting New Books.*

Telescopic Work for Starlight Evenings. By William F. Denning, *F.R.A.S.* (Taylor and Francis.)

UNIVERSALLY recognized as one of the greatest living authorities on the subject of Meteoric Astronomy, Mr. Denning has also discovered two comets, and made numerous and accurate

observations and drawings of planetary details and other celestial phenomena. For many years he has been a prolific writer in astronomical serials and the Proceedings of learned societies. A work from his *facile* pen will therefore be read with much interest and expectation by all lovers of the "sublime science." And his readers will not be disappointed. This is a very interesting and valuable work. Emanating as it does from a distinguished astronomer, and founded as it is on the results of the author's practical experience, it is of course worthy of more attention and confidence than books which are merely compilations from the writings and observations of others.

The book opens with an interesting chapter on the invention and development of the telescope. The second chapter discusses the relative merits of large and small telescopes, in which it is clearly shown that the utility of small instruments is not to be despised. The author thinks that future development in telescopes will take place in the size of reflectors rather than in refractors, which have now nearly reached their limit of aperture, and in this conclusion he is most probably correct. In Chapter iv. most useful hints are given to the amateur observer on telescopic observations, and the best methods of arriving at useful results. Mr. Denning very justly says (p. 78), "Some amateurs take an incredible amount of pains to look up an object for the simple satisfaction of seeing it. But seeing an object is not observing it. The mere view counts for nothing from a scientific standpoint, though it may doubtless afford some satisfaction to the person obtaining it"; and again (p. 81), "It need hardly be said that every difficulty may be surmounted by perseverance, and that a man's enthusiasm is often the measure of his success, and success is rarely denied to him whose heart is in his work."

Interesting chapters follow on the Sun, Moon, Planets, and Comets, and contain much information and many useful practical hints. The chapter on "Meteors and Meteoric Observations" is, as might be expected from Mr. Denning, especially good.

The concluding chapters of the work treat of the Stars, Nebulæ, and Clusters. These include some useful tables of some remarkable objects; but the list of variable stars is rather short, some interesting objects—for instance R Leonis—being omitted. In a second edition this list might with advantage be extended to, say, two pages instead of one.

It is the duty of a reviewer to look for misprints and errors in the book he reviews. Mr. Denning's book has passed through this ordeal very satisfactorily. Of misprints none have been detected. Of inaccuracies there are very few. On p. 114 the moon's mean distance is given as 237,000 miles. This should be 238,800 miles. Mann's orbit for Sirius, referred to on p. 307, is now known to be incorrect. The companion has certainly not yet passed through the periastron, and probably will not do so for a few years to come. In the List of Variable Stars, p. 311, the minimum of *o* Ceti is given as 0, or complete invisibility even with a telescope. This is

incorrect, as the star never descends below magnitude $9\frac{1}{2}$, and in fact always remains visible in a telescope of 3 inches aperture, or even 2 inches. The minimum of η Argûs is given as 6 magnitude; but the star has been seen as faint as $7\frac{1}{2}$ (in 1886), and is at present about the 7th magnitude. Its period, if it has one, has not yet been satisfactorily determined. These are trivial matters, however, and do not detract from the value of a book which it is to be hoped will meet with the success it deserves. All telescopists should procure a copy of the work without delay. The book is well printed and bound, and contains numerous excellent illustrations.

J. E. Gore.

A Treatise on Analytical Statics, with numerous examples. By E. J. Routh, *Sc.D., F.R.S.* Vol. I. (Cambridge: University Press, 1891; pp. xii+407.)

We approach this new work by Dr. Routh as if it were the work of a "blessed Glendoveer" ("'tis mine to speak, and yours to hear"). We never had the good fortune to sit at his feet and so have had a more thorough enjoyment in reading it than any one of his numerous "sons" who are familiar with his methods can have. He himself opens his preface with the words: "During many years it has been my duty and pleasure to give courses of lectures on various mathematical subjects to successive generations of students. The course on Statics has been made the groundwork of the present treatise. It has, however, been necessary to make many additions; for in a treatise all parts of the subject must be discussed in a connected form, while in a series of lectures a suitable choice has to be made." We trust that Dr. Routh will not only complete his work on Statics, of which this is a first instalment, but also, in due time, give students the results of his many years' labours in other parts of the mathematical curriculum. Our author's mode of procedure is to "examine first how the elementary principles of statics are connected with the axioms required for the more general problem of dynamics, and secondly how they may be made to stand on a base of their own." J. Walsh wrote to De Morgan: "In mechanics the parallelogram of forces is quackery, and is dangerous; for nothing is at rest, or in uniform, or in rectilinear motion, in the universe. Laplace's demonstration of the parallelogram of forces is a begging of the question"*. Dr. Routh gives both Newton's and Duchayla's proofs. We do not intend, however, to go through the treatise in detail. The matter and the manner happily call for no comments of ours, we propose only to indicate what facts are taken up in this first instalment. Chapters i. to iv. take us through the elementary portions, such as forces acting at a point, parallel forces (theory of couples), forces in two dimensions, illustrated by a store of carefully selected examples, many worked out and others with pregnant hints for their solution. Chapter v. discusses friction;

* 'Budget of Paradoxes,' p. 155.

Chapter vi. the principle of work, here we have an account, with examples, of Rocking Stones, which it will be remembered the author has also treated in his Rigid Dynamics. In Chapter vii., on forces in three dimensions, we have an account of much that is given in Sir R. S. Ball's work on screws, and which will put the student into a position to profit by a study of that treatise. Chapter viii. is devoted to graphical statics and the consideration of Maxwell's and Cremona's theorems. Centres of gravity fill up Chapter ix.; and the fullest treatment we have met with of strings occupies Chapter x. The machines are rapidly gone through in Chapter xi. The fact of the text being grounded on successive annual courses of lectures readily accounts for Dr. Routh's great skill in meeting the difficulties which occur to students, and the result is a work which few will be able to pass over without loss. The practice has been kept up of referring "each result to its original author." It is a pity one cannot do this for so many of the beautiful problems in which the College papers abound. The printing matches the text, but two figures (pp. 58 & 275) are incorrectly drawn. We have noticed only five small mistakes besides the few pointed out in the errata. The only evidence of haste appears to be in the numerous cases towards the end of the book where after questions we have "May Exam.," "Coll. Exam.," "Tripos Exam.," and the like, whereas in the greater part of the work we have, as we ought to have, the "year" or the name of the College.

The Foundations of Geometry. *By* Edward T. Dixon. (Cambridge: Deighton, Bell, & Co., 1891; pp. viii + 143.)

Mr. Dixon in the treatise before us does not provide milk for babes, but strong meat for adult geometers. So he does not enter upon "the question whether beginners could readily be brought to understand his book or not." This inferior matter is postponed until his present reasoning is admitted to be sound. We have read all with great interest and can certainly commend the "foundations" to authors, teachers, and all other students of geometry, bar the babes, for in it they will find many valuable suggestions and acute criticisms. The author has rightly stated that "the crux of my theory lies in my definition of direction, for it has been chiefly owing to the want of such a definition that all previous attempts to make use of direction in Elementary Geometry have failed." We give here the implicit definition of Direction: "(*a*) a direction may be conceived to be indicated by naming two points, as the direction 'from one to the other.' (*b*) If a point move from a given position constantly in a given direction, there is only one path, or series of positions, along which it can pass. (Such a path is called a 'direct path,' and a continuous series of points occupying all positions in it, is called a 'straight line.') (*c*) If the direction from A to B is the same as that from B to C, the direction from A to C is also that same direction. (*d*) If two unterminated

direct paths, which intersect, are each intersected by a third direct path in two separate points, any unterminated direct path extending in the same direction as the last one, which intersects one of the two former, will also intersect the other." There are besides three axioms: on the possible transference of geometrical figures, the possible extension of a straight line and the three-way extension of space, but the *implicit* definition we have quoted above *in extenso* is the crucial point in the theory. Our readers are now furnished with the key to Mr. Dixon's method, and, whether they agree with him or not, they will find much of interest in this elaboration of his argument. In Part i. he writes on the Logical Status of the Science of Geometry. In Part ii. we have a subjective Theory of Geometry deduced from the two fundamental Concepts, Position and Direction. Herein the student is carried through the equivalent of great part of Euclid's books i. and xi. with the exceptions of those propositions in book i. which deal with plane areas. Part iii. dilates on the applicability of the foregoing subjective geometry to the geometry of material space. This contains some very interesting remarks upon what Mr. Dixon prefers to call "Geometry of four independent directions" in place of the common "Geometry of four dimensions," and an account of a method of forming diagrams in material space which are "orthogonal projections of the true figures" (p. 101). The printing is very well done and the figures are good and clear. We have detected only three typographical errors, one being "Faucoult's" pendula (p. 22); and on p. 53 occurs the funny expression "a cornery path."

Explication de l'époch Quaternaire sans Hypothèses.
Par H. Hermite. Neuchâtel, Attinger Frères, Éditeurs. 1891.

To anyone who has speculated on the causes of geological epochs the title of this work is calculated to raise an incredulous smile. That a period the characteristics of which are themselves more or less matters of surmise can be explained without recourse to hypotheses seems impossible. A careful perusal has not shown us that M. Hermite performs his promise, for a greater collection of unsupported assumptions it would be difficult to find put together.

The author commences by attempting to show that the figure of the earth is not an ellipsoid of revolution on the assumption of homogeneity, and that Newton's calculations give a larger equatorial diameter compared to the polar diameter than measurement has proved to exist.

By what he calls "the principle of the Equilibrium of the Seas," he thinks that this difference between theory and observation can be explained. We confess our inability to follow the reasoning by which he arrives at this conclusion; but it is connected with the greater salinity, and, as he thinks, consequent density of the seas at the Equator than at the Poles. But he takes no account of the

difference of temperature which acts in the opposite direction. He even suggests that the pronounced flattening of the poles of the planet Jupiter may be caused by the excess of salinity of its equatorial water. His conclusions on the Equilibrium of the Seas are summed up in these words:—"We see then, without striving at too much precision, *that to a diminution of the density of the seas corresponds a lowering of their surface.*" This is certainly the opposite of what we should expect, but how there could exist any great permanent difference of level in a fluid having free communication it is difficult to understand. This great principle of the equilibrium of the seas being established to the author's satisfaction, he goes on to explain the origin of the Quaternary Rains. Most English geologists are disbelievers in the excessive rainfall supposed by some to have distinguished the Quaternary climate, but the author takes the great precipitation as an established fact, and proceeds to explain it, as he seems to imagine, "without hypothesis."

The explanation is the greater prevalence of Volcanic energy from the Tertiary period gradually diminishing to the present time. These Tertiary and Quaternary volcanoes emitted vast quantities of steam saturating the atmosphere with vapour, which, being condensed by admixture of air from the seas, supplied the enormous rainfall M. Hermite considers necessary to hollow out the river-valleys as they now exist. These great rains were the cause of vast detrital deposits, which, collecting in basins, pressed down the Earth by their weight, as supposed by many other geologists of the present day. M. Hermite, who disbelieves in central heat, is, however, singular in accounting for the increase of heat downwards in the Earth's crust by the mechanical work done on the lower beds by the bulging caused by these sedimentary loads. Another and important effect of this bulging is to create faults and fissures, which allow the sea-water to penetrate to and ignite hypothetical beds of iron pyrites, creating volcanoes, which again are the cause of the immense Quaternary Rainfall, and so on *ad infinitum*, in a sort of cycle of perpetual motion. The later phenomena of Quaternary times, such as parallel terraces or raised beaches, are accounted for by the author's great principle of the equilibrium of the seas. The Quaternary precipitation being excessive reduced the density of the polar water. Every such variation made itself felt by the surface of the sea sinking when the water was fresher, and therefore less dense, or rising when or where more saline and denser. The parallel terraces, which are frequent at the poles and absent at the equator, are supposed to be records of the changes in the equilibrium of the seas.

The whole plan and scope of the work is so at variance with what English geologists have been taught to consider the true principles of Geology, that it would be a waste of space to give further examples of what the author perhaps is alone in thinking is an explanation of the Quaternary Epoch without hypothesis.

XXI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxxi. p. 441.]

March 11, 1891.—Dr. A. Geikie, F.R.S., President, in the Chair

THE following communications were read :—

1. "Manod and the Moelwyns." By A. V. Jennings, Esq., F.L.S., F.G.S., and G. J. Williams, Esq., F.G.S.

The area described by the authors is on the N. side of the Merionethshire anticlinal of Lower-Cambrian rocks, and contains Lingula Flags, Tremadoc and Arenig rocks. The authors correct what they think is an inaccuracy of some importance in the correlation of beds in different parts of the range, as interpreted in the map and memoir of the Geological Survey, and trace with greater completeness the position and constancy of the beds of slate in the Arenig series—a point of considerable local and practical importance to those engaged in slate-quarrying. They offer also what seems to them to be conclusive evidence to show the intrusive nature of the great crystalline mass known as the syenite of Tan-y-Grisiau, and to its intrusion are due, in their opinion, the peculiar physical characteristics of the surrounding country. Though in the immediate neighbourhood of Festiniog there is no direct evidence of unconformity between the Tremadoc and Arenig series, it seems probable that an unconformity does exist; for when traced toward the west the Tremadoc beds thin out and the Lingula Flags are overlain by graptolite-bearing slates of Arenig age, while eastward, near Llyn Serw, the grit comes close upon Upper-Lingula Flags. The division of the Arenig volcanic rocks into Lower Ashes, Felstone, and Upper Ashes, while true of some districts and useful as a generalization, conveys an idea of uniformity of strata all round the Anticlinal which more detailed examination of different districts does not support.

2. "The Tudor Specimen of *Eozoon*." By J. W. Gregory, Esq., F.G.S., F.Z.S.

March 25.—Dr. A. Geikie, F.R.S., President, in the Chair.

The following communications were read :—

1. "Notes on Nautili and Ammonites." By S. S. Buckman, Esq., F.G.S.

2. "On the Drifts of Flamborough Head." By G. W. Lamplugh, Esq., F.G.S.

The author describes in detail the characters and distribution of the glacial deposits on Flamborough Head, and classifies them as follows :—

Alluvial wash, freshwater marls, &c.	Recent.
Late glacial gravels	Glacial.
Upper Boulder Clay	
Intermediate Series. Stratified beds with bands of Boulder Clay	
Basement Boulder Clay	
Chalky rubble	

"Infra-glacial" beds of Sewerby and Speeton.

He discusses their relationship with other drifts, and arrives at the following conclusions:—

1. The glacial deposits are divisible into Upper and Lower Boulder Clay, with an Intermediate series.

2. The Lower Clay is a continuation of the Basement Clay of Holderness, and is the product of the first general glaciation of the area. The Intermediate series passes laterally into the Purple Clays of Holderness, and has been deposited at the edge of the ice-sheet. The Upper Clay includes the Hessle Clay of Holderness, and marks the latest glaciation of this region.

3. The fossiliferous beds of Sewerby ("Buried-cliff Beds") and Speeton ("Estuarine shell-bed") are older than the Basement Clay, and therefore than the earliest glaciation.

4. The glaciation was effected by land-ice of extraneous origin, which moved coastwise down the North Sea, and did not overflow the greater part of the Yorkshire Wolds.

5. Neither the Boulder Clays nor the Intermediate gravels are of marine origin, the shells which occur in them being derivative.

6. The ice-sheet seems to have filled the North-Sea basin in this latitude from the commencement of the glaciation until its close. There is no clear evidence here for a mild interglacial period, but only for extensive fluctuations of the margin of the ice.

3. "On a Phosphatic Chalk with *Belemnitella quadrata* at Taplow." By A. Strahan, Esq., M.A., F.G.S.

Two beds of brown chalk in an old pit near Taplow Court owe their colour to a multitude of brown grains. These grains are almost entirely of organic origin, foraminifera and shell-prisms forming the bulk of them. Mr. Player has analysed specimens of the brown chalk, and finds that it contains from 16 to 35 per cent. of phosphate of lime. The tests as well as the contents of the foraminifera seem to have been phosphatized, the phosphate appearing as a translucent film in the former case, and as an opaque mass in the latter. In the case of the prisms of molluscan shells, the whole of the phosphate appears to be in the opaque form. Minute coprolites also occur, together with many small chips of fish-bone, in which Dr. Hinde has recognized lacunæ, while some have been identified by Mr. E. T. Newton as portions of fish-teeth.

Mr. Player observes that the phosphate occurs in such a condition that it would not improbably serve as a valuable fertilizer, without conversion into superphosphate. This condition is probably due to the partial replacement of carbonate of lime by phosphate in the organisms. The removal of the remaining carbonate leaves the phosphate in a honeycombed state, peculiarly favourable for attack by the acids in the soil.

The author comments upon the resemblance of the deposit to the phosphatic chalk with *Belemnitella quadrata* which is largely worked in Northern France, and upon a less striking resemblance with that of Ciply, which is at a higher horizon.

April 8.—Dr. W. T. Blanford, F.R.S., Vice-President, in the Chair.

The following communications were read:—

1. "The Cross Fell Inlier." By Prof. H. A. Nicholson, M.D., D.Sc., F.G.S., and J. E. Marr, Esq., M.A., Sec.G.S.

The tract of Lower-Palæozoic rocks lying between the Carboniferous rocks of the Cross-Fell range and the New Red Sandstone of the Eden Valley is about sixteen miles in length, and little more than a mile in average breadth; the Inlier extends in a general N.N.W. and S.S.E. direction, and the normal strike of the rocks is about N.W. and S.E. The tract is divided along its entire length by a fault, which separates the Skiddaw Slates (with the Ellergill Beds of one of the authors and the Milburn Series of Mr. Goodchild) from higher beds on the west. A detailed classification of the Skiddaw Slates is not attempted, but the authors describe the succession of the rocks in the faulted blocks of the western portion. Their classification is as follows:—

Coniston Grits = Ludlow.
Coniston Flags (lower portion) = Wenlock.
Stockdale Shales = Llandovery-Tarannon.
Ashgill Shales.)
Staurocephalus Limestone. |
Dufton Shales and Keisley Limestone. > = Bala.
Corona Beds. |
Rhyolitic Group.)

A brief comparison of these rocks with those of other regions is made by the authors.

Two Appendices are added. One by Mr. Alfred Harker, M.A., F.G.S., contains petrographical notices of certain sedimentary and volcanic rocks in the Skiddaw Slates, of the volcanic rocks of the Eycott and Rhyolitic groups, and of the principal varieties of intrusive rocks. The second, by Mr. A. H. Foord, F.G.S., contains a description of some Cephalopods from the rocks of the Inlier.

2. "On the Igneous Rocks of the South of the Isle of Man." By Bernard Hobson, Esq., M.Sc., F.G.S.

Omitting the Foxdale Granite, the oldest igneous rocks of the island appear to be the diabase dykes of Langness &c., intrusive in Lower-Silurian slates. The Crosby microgranite dyke is also intrusive in these beds, and though its age is difficult to fix, it is probably newer than the Foxdale Granite, which appears to be of post-Lower Silurian and pre-Carboniferous age.

Next come the volcanic rocks of Lower-Carboniferous age—an augite-porphyrite series consisting of tuff, breccia, agglomerate, bedded lava, and intrusive masses exposed in a narrow strip extending from Poolvash to Scarlet Point. A vent seems to have been opened during or after the deposition of the Poolvash limestone, from which fine volcanic ashes were ejected to form marine tuff. At intervals between the eruptions the Poolvash marble was deposited, and became interstratified with the tuff. The vent then probably became plugged up, and a violent explosion

following supplied material for the agglomerate overlying the tuff. Lava then welled forth, and finally the volcano became extinct, and the intrusive mass of the Stack, regarded by the author as a volcanic neck, was exposed by denudation. It was probably at the close of volcanic activity that a melaphyre dyke was formed resembling the porphyritic olivine-basalt of the Lion's Haunch, Edinburgh.

At Poortown an intrusive mass occurs, provisionally termed augite-picrite-porphyrite, and considered by Mr. J. G. Cumming to be of post-Carboniferous age.

Numerous dykes of ophitic olivine-dolerite occur between Bay-ny-Carrickey and Castletown Bay, at Langness, &c. They are post-Lower Carboniferous, and possibly of early Tertiary age.

Full details with regard to the development and the macroscopic and microscopic characters of the various igneous rocks are supplied by the author, who acknowledges his indebtedness to Prof. Boyd Dawkins for the use of his geological map and notes.

April 22.—Dr. A. Geikie, F.R.S., President, in the Chair.

The following communications were read:—

1. "Results of an Examination of the Crystalline Rocks of the Lizard District." By Professor T. G. Bonney, D.Sc., LL.D., F.R.S., V.P.G.S., and Major-General C. A. McMahon, F.G.S.

The authors, in company with the Rev. E. Hill, spent a considerable part of last August in examining anew those sections in the Lizard district which had any bearing upon the questions raised since the publication of Professor Bonney's second paper in 1883. They had also the advantage of occasional conference with Mr. Teall and Mr. Fox, whose valuable contributions to the knowledge of the crystalline rocks of this district are well known.

That the Lizard serpentines are altered peridotites may be regarded as settled, but doubts have been expressed as to their relation to other associated rocks, and as to the meaning of a streaky or banded structure exhibited by certain varieties.

The authors, after re-examination of a large number of sections, feel no doubt of the accuracy of their original view that the peridotite was intruded into the hornblende schists and banded "granulitic" rocks, after these had assumed their present condition. In it they find no signs of any marked pressure-metamorphism, either prior or posterior to serpentinization. They have failed to connect the streaky or banded structure with any foliation or possible pressure-structure in the schists, and they can only explain it as a kind of fluxion-structure, viz. as due to an imperfect blending of two magmas of slightly different chemical composition, anterior to the crystallization of the mass.

The Porthalla sections have been examined with especial care, not only because the serpentine is nowhere so conspicuously banded, but also because its intrusive character has been denied, both it and the hornblende schists being ascribed to the alteration of a series of sedimentary rocks of suitable composition. For this view the

authors have failed to discover any evidence, and consider it contrary to stratigraphical and petrographical facts.

In regard to the genesis of the crystalline schists, which for purposes of reference were divided by Prof. Bonney into a "granulitic," a "hornblendic," and a "micaceous" group, the authors show that in parts of the first the more acid rock breaks through the more basic, as if intrusive, in others they appear to be perfectly interstratified, the one passing backwards and forwards, though rapidly, into the other. But between these extremes, intervals can be found where the two rocks seem as if partially drawn out together. The authors are agreed that certainly one, probably both, of these rocks are igneous, that when the basic rock was solid enough to be ruptured the acid magma broke into it, and sometimes softened it sufficiently to allow of the two flowing for some little distance together, after which crystallization took place. In regard to the hornblende schists, the authors are not yet satisfied that either fluxion or mechanical crushing will account for every structure which they have examined, and prefer to leave the question, in certain cases, an open one. The most distinctive features of the micaceous group appear due to subsequent earth-movements, so that, though it exhibits some special characteristics, the authors are doubtful whether it is any longer worth while separating it from the hornblende schists.

Of the igneous rocks newer than the serpentine, the gabbro has received the closest attention. It exhibits in places (especially in the great dyke-like mass at Carrick Luz) a very remarkable foliation or even mineral banding, which has been claimed as a result of dynamo-metamorphism. The authors bring forward a number of instances to establish the following conclusions:—(*a*) That this foliation occurs most markedly where the adjacent serpentine does not show the slightest sign of mechanical disturbance; (*b*) that it must be a structure anterior to the consolidation of the rock; (*c*) that it sets in and out in a very irregular manner; (*d*) that when it was produced the rock was probably not a perfect fluid. Hence they explain it also as a kind of fluxion structure, produced by differential movements in a mass which consisted of crystals of felspar and pyroxene, floating thickly in a more or less viscous magma.

The authors' investigations tend to prove that (*a*) structures curiously simulative of stratification may be produced in fairly coarsely crystalline rocks by fluxional movements anterior to crystallization; and that (*b*) structures which of late years have been claimed as the result of dynamo-metamorphism subsequent to consolidation must have, in many cases, a like explanation. This is probably the true explanation of a large number of banded gneisses which show no signs of crushing and are holocrystalline, but in their more minute structures differ from normal igneous rocks.

The authors have seen nothing which has been favourable to the idea that pressure has raised the temperature of solid rocks sufficiently to soften them.

2. "On a Spherulitic and Perlitic Obsidian from Pilas, Jalisco, Mexico." By Frank Rutley, Esq., F.G.S.

The specimen described is a leek-green rock with waxy lustre.

The sequence of the structures developed in it is made out to be as follows:—First, the development of fluxion-banding; next, the formation of spherulites; and then the setting up of a perlitic structure, the fissures of which were finally sealed by the introduction of chalcedonic matter.

A wavy transverse banding in the spherulites is apparently due to a temporary check which the fluxion-bands have exerted on the development of the crystalline bundles of the spherulites. In one case a spherulite has been developed prior to the formation of a similar but larger one which encloses it. Some of the spherulites envelop small crystals of triclinic felspar.

The author considers it very probable that the obsidian has been subjected to hydrothermal agency since its solidification, and subsequent to the development of its perlitic structure, and gives reasons for this view.

May 6.—Dr. A. Geikie, F.R.S., President, in the Chair.

The following communications were read:—

1. "On a Rhætic Section at Pylle Hill or Totter Down, Bristol." By E. Wilson, Esq., F.G.S.

In a deep railway-cutting at Pylle Hill, the Rhætic beds, having a thickness of not more than seventeen feet, are exposed between the Tea-Green Marls and the Lower Lias. There is no doubt as to the division between the Rhætic and Keuper beds in this section, but the line of demarcation between the Rhætic and the Lias has always been a matter of uncertainty in the West of England. In connexion with this subject the term "White Lias," as applied to beds some of which are Rhætic and others Liassic, is held to be unsatisfactory. The author takes a limestone which is the equivalent of the Cotham Marble as the highest Rhætic bed in the section described. He divides the Rhætic beds of the cutting into an Upper-Rhætic Series and *Avicula-contorta* Shales. The intimate connexion betwixt the Tea-Green Marls and the Red Marls of the Upper Keuper is well displayed, whilst there is a sharp line of demarcation between the former and the *Avicula-contorta* Shales. Most of the characteristic fossils of the British Rhætic are met with at Pylle Hill, together with a few forms which are new to England, and some of these possibly to science.

A detailed section of the subdivisions of the Rhætic and adjacent beds and a list of Rhætic fossils found in the section are given by the author.

2. "A Microscopic Study of the Inferior Oolite of the Cotteswold Hills, including the Residues insoluble in Hydrochloric Acid." By Edward Wethered, Esq., F.G.S., F.C.S., F.R.M.S.

The author gives the following main divisions of the Inferior Oolite of the Cotteswold Hills in descending order:—

Ragstones.
Upper Freestones.

Oolitic Marl.
Lower Freestones.
Pea Grit.
Transition Beds resting on Upper Lias.

The strata are described, and the results of microscopic examination of the different beds given. These latter confirm the author's views as to the important part which *Girvanellæ* have taken in the formation of oolitic granules; whilst an examination of the borings referred to by Prof. Judd in the discussion of Mr. Strahan's paper "On a Phosphatic Chalk" convinces the author that these have no connexion with the genus *Girvanella*.

In the second part of the paper the insoluble residues left after treating the various deposits with acid are considered. They contain chiefly detrital quartz, felspars, zircons, tourmaline, chips of garnet, and occasionally rutile. In the argillaceous beds silicate of alumina was found to occur plentifully. The detrital material is considered to be due to denudation of crystalline felspathic rocks, and not of stratified ones. This view seems to be supported by the quantity of felspar and its good state of preservation.

The paper concludes with a consideration of the quantity of residue and the size of the quartz-grains in the different deposits, which are summarized in the following table:—

	Percentage of Residue.	Size of quartz-grains, in millim.
Ragstones	2·8	·17
Upper Freestones	1·1	·12
Oolitic Marl	3·2	·09
Lower Freestones	1·8	·13
Pea-Grit Series	5·0	·14
Transition Beds	38·3	·13

This shows a great falling-off in the percentage of residue above the Transition Beds. That of the Freestones is remarkably low, and it would appear that these rocks were formed under conditions which allowed of very little sediment being deposited.

May 27.—Dr. A. Geikie, F.R.S., President, in the Chair.

The following communications were read:—

1. "On the Lower Jaws of *Procoptodon*." By R. Lydekker, Esq., B.A., F.G.S.

2. "On some recently exposed Sections in the Glacial Deposits at Hendon." By Henry Hicks, M.D., F.R.S., Sec. Geol. Soc.

In this paper the author brings forward evidence obtained from sections exposed in gravel-pits and deep cuttings made for the purpose of laying down the main sewers, to show that Glacial deposits had been spread out to a much wider extent over the Hendon plateau than had hitherto been supposed, and that they had reached down the slopes to below the ordnance-datum line of 200 feet. He

further mentions that there is evidence to show that these deposits have extended in a S. and S.W. direction across the Brent and Silk Valleys, and now occur on most of the heights in the parishes of Kingsbury and Willesden. As the sands, gravels, and Boulder-clay which cover the Hendon plateau and the neighbouring heights are found to rest on an undulating floor of London Clay, and to follow the contours of the hills and valleys, the author considers that it is clear that the main physical features of this portion of N.W. Middlesex were moulded at a very early stage in the Glacial period, and before the so-called Middle sands and gravels and overlying Upper Boulder-clay with Northern erratics were deposited. He believes that at this time there could have been no barrier of any importance to prevent these deposits from extending into the Thames Valley, and that the evidence clearly points to the conclusion that the implement-bearing deposits on the higher horizons in the Thames Valley should be classed as of contemporaneous age with the undoubted glacial deposits at Hendon, Finchley, and on the slopes of the Brent Valley, which they so closely resemble. The author is therefore satisfied that man lived in the neighbourhood of the Thames Valley in the early part of the Glacial period; probably, he thinks, in pre-Glacial times.

June 10.—Sir Archibald Geikie, LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. "Note on some Recent Excavations in the Wellington College district." By the Rev. A. Irving, B.A., D.Sc., F.G.S.

This paper furnishes new facts of Bagshot stratigraphy obtained from open sections since the author's last paper was read on Nov. 12th, 1890. The whole sequence of the beds, as given in the published section of the College Well, has now been verified at their respective outcrops; percentages of clay in the beds laid open in excavations in March last along the critical portion of the ground are given as results of mechanical analyses of samples of them; and the northerly attenuation of the green-earth series and of the quartz-sand series is reduced to a question of mere measurement, for which the requisite data are now to hand.

The author claims to have demonstrated that the mapping of the Geological Survey contradicts itself: that later workers in adopting this as the basis of their work along the S.E. Railway have fallen into serious error; and that a complete contradiction is given by the facts to the adverse criticisms offered on his corrected section along the railway, which was exhibited in November last, and is reproduced for the present paper.

2. "Notes on some Post-Tertiary Marine Deposits on the South Coast of England." By Alfred Bell, Esq. Communicated by R. Etheridge, Esq., F.R.S., F.G.S.

The author's object in this paper is to trace the successive stages

in the development of the present coast of the north side of the English Channel, and to ascertain the sources of the diversified faunas.

The first traces of marine action on the South Coast in Post-Tertiary times are found on the foreshore in Bracklesham Bay. The author's reading of the section is somewhat different from that of the late Mr. Godwin-Austen; and he divides the marine series into (1) an estuarine clay with Mollusca common to estuarine flats; (2) a compact hard mud; and (3) a bed of fine sandy silt with many organisms. These beds indicate a change from estuarine to deep-water conditions. A full list of the Selsey fossils is given, including, amongst other animals, upwards of 200 Mollusca. Of 35 species of Mollusca not now living in Britain, the majority exist in Lusitanian, Mediterranean, or African waters; furthermore, nearly 45 per cent of the Mollusca are common to the older Crags of the Eastern counties. The author considers the fauna of the Portland Bill shell-beds to indicate the further opening of the Channel subsequent to the formation of the Severn Straits, and believes that this fauna represents the deposits wanting between the Selsey mud-deposits and the erratic blocks which, according to him, overlie the mud; these Portland shells indicate an intermediate temperature "rather southern than northern" according to Dr. Gwyn Jeffreys.

In conclusion, details concerning still newer beds are given, and lists of fossils found therein; and the author observes that there is no evidence to show when the English Channel finally opened up, beyond the suggestion of Mr. Godwin-Austen that, if the Sangatte beds and the Coombe Rock are of the same period, it must have taken place after their formation.

XXII. *Intelligence and Miscellaneous Articles.*

ON THE ANALYSIS OF THE LIGHT DIFFUSED BY THE SKY.

BY A. CROVA.

IN a preceding communication I gave* the results of my first researches on this subject, explained the method of observation, and discussed the curves obtained; in this note I resume the discussion of the results to which the method of calculation adopted has led me, and the comparison of the 1890 observations with those made before both in France and abroad.

The formula of Lord Rayleigh, deduced from Stokes's theory†, is

$$\iota = N\frac{a^2}{p^2\lambda^4},$$

in which ι is the intensity of the light diffracted by a point of the

* *Comptes Rendus*, xix. p. 493; *Ann. de Chim. et de Phys.* ser. 6, xx. p. 480.

† Phil. Mag. ser. 4, xli. p. 107 (1871).

sky, N the number of diffracting particles contained in unit volume of air, a the amplitude of the incident vibration of wave-length λ, and p a factor constant for all values of λ.

As the greater part of my observations could not be calculated by this formula, I have sought the reason for the disagreement.

The formula $\frac{1}{\lambda^4}$ is based on the hypothesis that the number N of particles contained in unit volume of air is sensibly the same for all dimensions of these; it will therefore not be verified unless this hypothesis is realized.

If we compare the particles to spherical globules of density D and with different radii r, falling in a medium of density ρ, they will take, at the end of a very short time, a constant velocity of fall in the resisting medium given by the formula

$$v = \sqrt{\frac{gDr}{\gamma\rho}},$$

γ being a factor which depends on the nature of the medium.

In air we should have

$$V = A\sqrt{r}.$$

If, at the beginning, the diffracting particles, equal in number for all dimensions of the same order as the λ's of the incident light, are uniformly distributed in the unit volume of air and left to themselves, they will take different velocities according to their dimensions, and we may assume that, when the permanent state is established, the number contained in unit volume varies, for each dimension of the particles, in the inverse ratio of the velocity; in this case we should have

$$N = \frac{B}{\sqrt{r}}.$$

Giving to r the extreme relative values 1 and 2 which correspond sensibly to the dimensions of the particles which diffract more especially the extreme wave-lengths of the spectrum; for the extreme red $N = \frac{B'}{\sqrt{r}}$ and for the extreme violet $N' = B'$.

We must then, in the preceding formula, replace N by $\frac{N}{\sqrt{r}}$ or by $\frac{N'}{\sqrt{\lambda}}$, and the formula becomes

$$\iota = \frac{N'}{\sqrt{\lambda}} \frac{D}{\lambda^4} = \frac{K}{\lambda^{4.5}}.$$

In reality we might found several hypotheses on this mode of distribution; $\frac{N'}{\sqrt{\lambda}}$ might be replaced by $N'f(\lambda)$, the function of λ depending on a certain power of the velocity, and consequently of the dimensions of the particles.

I have accordingly arbitrarily modified the exponent of λ in such manner as to make the results of observation agree with the formula $\frac{K}{\lambda^n}$.

Let B be the intensity of the blue light diffused by the sky and S the intensity of the incident solar light; then, putting the value of $\frac{B}{S}$ for $\lambda=565$ equal to 100, we shall have

$$\frac{B}{S}=\frac{K}{\lambda^n},\quad 100=\frac{K}{565^n},\quad \text{whence } \frac{B}{S}=100\left(\frac{565}{\lambda}\right)^n,$$

n being a coefficient which is calculated by means of the values of $\frac{B}{S}$ corresponding to fixed values of λ.

On differentiating we obtain

$$\tan\alpha=-100\,n\frac{565^n}{\lambda^{n+1}},$$

and for the common ordinate $=100$ which corresponds to $\lambda=565$

$$\tan\alpha_1=-\frac{100}{565}n;$$

n being therefore proportional to the angular coefficient at the point of intersection of all the curves which are obtained by making n vary, that is to say, to the inclination of the curve at that point.

I have compared the results calculated from the formulæ $\frac{1}{\lambda^4}$ and $\frac{1}{\lambda^{4\cdot5}}$ with those of the observations of Lord Rayleigh in England* and of Vogel† at Potsdam, as well as with some of the results of my observations at Montpellier.

In the former case, I have constructed the curves of these observations and have determined the values of the ordinates corresponding to

$$\lambda \ldots. \quad 635 \quad 600 \quad 565 \quad 530 \quad 510,$$

and traced a new curve for which the ordinate corresponding to $\lambda=565$ has been arbitrarily made $=100$.

For the series of M. Vogel, who gives, not $\frac{B}{S}$, but $\frac{B}{P}$, that is to say the ratio of the intensity of skylight to that of petroleum, I have divided the ratios $\frac{B}{P}$ by those of $\frac{S}{P}$ or of the intensity of solar light to that of petroleum for the different λ's found by M. Vogel, which gives the corresponding values of $\frac{B}{S}$, and I have reduced the

* Phil. Mag. ser. 4, xli. p. 107.
† *Berl. Monatsber.* pp. 801–811.

curve to that which corresponds to an ordinate $=100$ for $\lambda=565$. All these curves are therefore comparable:

λ.	635.	600.	565.	530.	510.
$100\left(\frac{565}{\lambda}\right)^4$	62·68	78·63	100	128·1	150·6
$100\left(\frac{565}{\lambda}\right)^{4\cdot5}$	49·73	69·73	„	146·7	180·7
$100\frac{B}{S}$ (England).....	58·59	78·55	„	130·3	151·4
$100\frac{B}{S}$ (Potsdam).....	63·00	76·00	„	126·0	146·0
$100\frac{B}{S}$ (Montpellier, mean of Jan. 1890).	58·30	76·47	„	141·1	180·8
100 (Montpellier, mean of 1890).....	„	71·31	„	130·0	„

We see, by a simple inspection of this table:—

(1) That in England the blue of the sky observed by Lord Rayleigh is more saturated than that which was observed at Potsdam by M. Vogel: it agrees sufficiently with the formula $\frac{1}{\lambda^4}$ while giving a little deeper blue.

(2) That the blue of the sky observed at Montpellier, during the month of January 1890, is deeper than those observed in England and in Germany, and that it approaches more nearly the formula $\frac{1}{\lambda^{4\cdot5}}$.

I give below, as an example of the application of this method, the formulæ which give the value of $100\frac{B}{S}$ for three observations made by M. Houdaille and myself at the summit of Mt. Ventoux:

Aug. 3, 1889, $10^h\ 40^m$ .. $\frac{B}{S}=100\left(\frac{565}{\lambda}\right)^{5\cdot75}$. Sky of a clear blue.

Aug. 3, 1889, 10 20 .. $\frac{B}{S}=100\left(\frac{565}{\lambda}\right)^{2\cdot55}$. Sky of a clear blue.

Sept 3, 1889, 9 40 .. $\frac{B}{S}=100\left(\frac{565}{\lambda}\right)^{6\cdot44}$. Sky of a deep blue.

The differences between the values found and calculated are of the order of errors which might be made in photometric observations; they are sometimes augmented in consequence of the extreme variability of the blue tint of the sky under the influence of causes most insignificant in appearance.—*Comptes Rendus*, May 25, 1891, p. 1176.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

AUGUST 1891.

XXIII. *Chemical Action at a Distance.* *By* Prof. W. OSTWALD*.

A PIECE of amalgamated zinc, as is well known, is not attacked by dilute acids; if, however, a platinum wire be wound about it, solution in the acid takes place at once with evolution of hydrogen. Zinc, armed with platinum, cannot be dissolved in solutions of neutral salts, as, for instance, potassium sulphate; if a few drops of acid, as sulphuric acid, be added to the liquid, solution again ensues.

For the platinum to exercise its action, it is only necessary that it remain in contact with the zinc at a single point. If zinc and platinum be made into a curved piece, with its arms some slight distance apart, and these be so placed in a potassium-sulphate solution that the portions of the liquid surrounding each arm are separated by a wall of porous material, such as unglazed earthenware or parchment-paper, then the question can be decided which metal, zinc or platinum, must come in contact with the acid that solution may result.

At first sight the question seems absurd; for since the zinc is to be dissolved, it seems self-evident that the acid belongs with the zinc. However, if the experiment be tried, one finds exactly the reverse: the zinc does not dissolve (with the exception of traces which would go into solution in any event) when the potassium-sulphate solution about it is acidified; it

* From the *Sitzungsberichte der Kgl. Sächsischen Gesellschaft der Wissenschaften* for 1891, communicated by the Author. Translated by J. E. Trevor.

is rapidly dissolved, on the contrary, with evolution of hydrogen, when the liquid about the platinum is acidified. The hydrogen appears on the platinum, as it always does when these two metals are in contact. In order, under the described conditions, to bring the zinc into solution, the solvent must be allowed to act, not upon the metal to be dissolved, but upon the platinum which is connected with it.

Zinc behaves in a solution of common salt in exactly the same way as in one of potassium sulphate; cadmium shows the same behaviour. Tin is quite easily dissolved in a solution of common salt when the metal is connected with platinum and the liquid about the latter is acidified. Yet in a solution of potassium sulphate, tin armed with platinum is dissolved, even with the aid of sulphuric acid, but very slowly, just as this metal alone is attacked only in slight degree by dilute sulphuric acid. The behaviour of aluminium is similar to that of tin; yet the experiments therewith are not so striking, because with a neutral solution of common salt it develops bubbles of hydrogen upon its own surface (which is presumably to be referred to the carbon contained in the metal); still, at least, solution takes place far more rapidly when the solution of salt is acidified at the platinum. In potassium sulphate also there ensues almost no solution upon acidifying at the platinum, just as dilute sulphuric acid scarcely acts upon aluminium.

The phenomena described agree in this, that the metals in question when brought, in contact with platinum, into neutral salt-solutions, are dissolved when the ordinary solvents of these metals are allowed to act upon the platinum. It may be asked whether the metals which are dissolved, not with evolution of hydrogen, but only with the accompanying action of an oxidizing agent, may be brought into solution according to the same fundamental principle. Experiment answers this question affirmatively; even the more resisting metals, when connected with platinum, upon which their specific solvent is allowed to act, are dissolved in liquids which otherwise never attack them.

So, for instance, after a few minutes one finds considerable amounts of *silver* dissolved in dilute sulphuric acid, when the metal has been connected with a platinum wire near which a few drops of chromic-acid (or potassium-bichromate) solution have been added to the sulphuric acid. At the same time every caution may be employed to protect the silver from contact with the chromate, and yet the action will be found: the experiment decides unequivocally that the contact of the platinum with the oxidizing agent conditions the dissolving

action. Similarly silver can be dissolved in a solution of sodium acetate.

In the same way gold may be dissolved in a solution of common salt, when the platinum is brought in contact with chlorine (with a salt-solution saturated with chlorine). After but two or three minutes, in the solution which surrounds the gold, the characteristic reactions of this metal with ferrous sulphate or stannous chloride may be obtained.

I have for the most part carried out the experiments briefly described here by bringing into a small beaker an open short tube of about 2 centim. diameter, closed below with parchment-paper, and then filling both with the indifferent liquid, taking care at the same time to have the level in the tube always above that in the beaker. In the tube was placed the metal to be dissolved, the platinum wire connected therewith went to the bottom of the beaker. The solvents added were so chosen that they were heavier than the indifferent liquid; when a few drops thereof were brought with a pipette upon the bottom of the outer vessel they remained lying there without approaching the parchment-paper partition, which remained in the upper part of the liquid. After the close of the experiment the contents of the glass could then be easily investigated.

These phenomena, which were in part already known, I have termed chemical action at a distance; because the appearance in every case is as if the specific solvent of the the metals, when applied at the platinum, exercises its action at a distance upon the metal in question. As concerns the explanation, therefore, there can plainly be no doubt that the electrolytic relations play here the decisive role. In fact the simplest means of deciding whether solution ensues or not is to switch a moderately sensitive galvanometer into the circuit between the metal and the platinum. While compounds which exert no action give a current of only short duration, which falls at once to a very slight amount, addition of the acting substance (acid or oxidizing agent) to the platinum causes at once a strong deflexion of the needle. No deflexion, on the contrary, is observed when the acting substance is brought into contact with the metal to be dissolved.

As before mentioned, certain phenomena of this kind are already known. Thomsen, thirty years ago*, described a galvanic element which consists of copper in dilute sulphuric acid and carbon in a chromate mixture; on closing the connexion by means of a conductor between the copper and the carbon, the metal, which alone is not soluble in sul-

* Poggendorff's *Annalen*, cxi. p. 192 (1860).

phuric acid, goes into solution as sulphate. It is also known that the solution of zinc and similar metals in dilute acids is extremely accelerated by the presence of "electronegative" metals, and the text-books with the mention of this fact do not neglect to emphasize the "galvanic contrast" which conditions the effect. Yet I do not know that an attempt at a closer analysis has been made, an effort in the direction of an explanation of the way in which the "galvanic contrast" can produce such action. In fact these actions, like so many others, seem to belong with those for which a satisfying explanation can be first gained on the ground of the *Theory of free ions*, of Arrhenius. They then assume the following form.

Assume a metal, as zinc, to be in contact with the solution of an electrolyte, as potassium sulphate. The zinc may only go into solution by its atoms becoming loosened from the metal in the form of ions with their corresponding charges of electricity. In what manner this charging with electricity takes place, and in what it consists, are questions which we cannot at present answer; but since by taking positive electricity from the ions of the metals we can get the latter with their familiar properties again, we are justified in looking upon the taking up of positive electricity as the characteristic of the transition of a metal into the condition of ions.

As positive ions leave the originally neutral zinc, the latter becomes charged negatively and the solution positively. This lasts until a certain definite difference of potential has been established between the metal and the solution, according to which just as many positive ions are attracted out of the solution by the negative charge of the metal, as go into the solution as a result of the "solution-tension" of the zinc*; then equilibrium occurs. On account of the very great quantities of electricity carried by the ions the necessary quantities of metal are extremely slight, in general too slight to be shown by analytical tests.

The zinc is accordingly hindered from further solution by the excess of positive ions which exists in the liquid, and in order to make further solution possible these ions must be removed. If another metal, for example platinum, be connected with the zinc, this assumes the same negative charge as the zinc. If the platinum be dipped into the liquid this negative charge acts electrostatically upon the excess of positive ions, and these collect at the platinum.

Now the facts of galvanic polarization show that the elec-

* Refer to W. Nernst, *Zeitschrift für physikalische Chemie*, iv. p. 150 (1889).

trical charge can only be directly removed from the ions when they come into contact with electrodes of the same nature. According to the present condition of our knowledge this occurs only in cases of positive ions, which consist of metal atoms, in contact with electrodes of the same metal. A system, for example, of two zinc plates in zinc-sulphate solution allows the weakest galvanic current to pass through and takes up no charge (not considering the secondary actions from alterations in concentration, which do not concern us here); while, for example, a system of two platinum plates in dilute sulphuric acid allows a continuous current to pass only upon the application of electromotive forces of definite amount (over 1·8 volt), after a not inconsiderable quantity of electricity has gathered upon the plates in the form of a charge. We must conclude from this that, for the transfer of electricity from an ion to a heterogeneous electrode, a definite difference of potential is in general requisite, which is to be regarded as dependent upon the nature of the ion as well as upon that of the electrode.

To return to the above-mentioned case, it will depend upon the nature of the positive ion and of the electrode whether the former, under the influence of the difference of potential caused by the presence of the zinc, will give up to the platinum its electricity or not. If the ion be the potassium of potassium sulphate, which holds the electricity very firmly and only gives it up under the action of potential differences of between two and three volts, no transfer of the electricity will take place. If, however, the potassium sulphate *at the platinum wire* be replaced by sulphuric acid, the difference of potential then at hand is sufficient to force the hydrogen ions thereof to part with their electrical charges, whereupon they escape in the form of ordinary hydrogen. By the combination of this positive electricity with the negative of the metal the latter is partially neutralized, the zinc, in consequence of its lowered negative potential, becomes able to send out more positive ions, and the action continues as long as metallic zinc or hydrogen ions remain at disposal.

This explanation makes apparent why in this case the acid must be at the platinum and not at the zinc; it throws light at the same time upon all the peculiarities which are manifested when zinc is dissolved in acids, and which have till now remained insufficiently explained. It forms at the same time the starting-point towards an understanding of the phenomena connected with the dissolving of the metals in general.

Pure zinc does not dissolve in acids, as was found by De

la Rive; well amalgamated zinc has the same property. The metal does not have, in this case, less tendency to go into solution than when impure; for if it be connected with platinum, copper, or any other similarly acting metal, solution at once ensues. The difficulty lies, therefore, plainly not in the *dissolving of the zinc*, but in the *evolution of the* hydrogen; when this latter action is assisted the solution takes place, in the case of either pure or amalgamated metal. That the hydrogen is evolved with difficulty at the zinc, more readily at the so-called negative metals, lies in the differences of potential towards the electrolyte. Zinc has a strong, positive solution-tension, that is it sends positive ions readily into the liquid and opposes correspondingly the reverse action, the reception of positive hydrogen ions and the removal of their charges. The other metals in contact with the same electrolyte develop a far less difference of potential, or possibly one of opposite sign, and either offer far less resistance to the discharging of the hydrogen or even assist it.

This is the reason why zinc dissolves in acids when in contact with other metals; it is clear that the usual form of expression, that solution takes place *in consequence of* galvanic currents between the zinc and the other metals, does not entirely correspond to the facts of the case. The galvanic currents are indeed inseparably connected with the act of solution; they are, however, not the primary agent which effects solution, but are produced by the act of solution which they must necessarily accompany, because the question is one of the formation and displacement of ions. Solution ensues when the possibility is present that the positive ions in the solvent may in any way be removed therefrom.

Differing from the simple displacement of positive ions, as in the case of zinc (as also magnesium, cadmium, and a few other metals), the dissolving of such metals as are not able to effect this displacement is accomplished by means of the *destruction of positive ions*, or what has the same effect, the *creation of negative ions*. Both are accomplished by the action of oxidizing agents, the first by means of reactions which produce non-electrolytes, the second by such as produce electrolytes.

An example of the first case is the dissolving of copper in dilute sulphuric acid, which takes place slowly under the action of free oxygen. Here the hydrogen ions of the acid combine with the oxygen atoms to form the non-electrolyte water, and thereby it becomes possible for a corresponding number of copper ions to be formed, that is for the copper to go into solution.

An example of the second case is the dissolving of gold in chlorine-water. In order that gold ions may enter the liquid there must be formed there a corresponding number (three times greater) of chlorine ions; this takes place by the splitting up of the chlorine molecules of the chlorine-water into negatively charged chlorine ions.

The closer analysis of these reactions leads us consequently to conclusions by which certain assumptions in regard to the electrical charges of the atoms suffer not inconsiderable changes. Since the time of the electrochemical theory of Berzelius the idea has been held that the holding together of the atoms in molecules is conditioned by the opposed electrical charges of the former, and this representation has been also applied to the case of the combination of the *same* atoms, which Berzelius looked upon as impossible. According to this a neutral chlorine molecule would have to yield a positive and a negative chlorine atom when split up. But such an assumption stands in complete contradiction with experience, which has hitherto made us acquainted with negatively charged chlorine atoms exclusively, and we have not the slightest indication that positive chlorine ions can exist. We must, on the contrary, in the face of the entirely general fact of the formation of dissociated chlorides out of the metals and free chlorine, make the assumption that with the breaking down of the chlorine molecules Cl_2 into chlorine ions (not *chlorine atoms*, as are formed at white heat) both parts of the molecule assume the same negative charge. This seems to stand in opposition to the general experience that, with the formation of electrical charges, equal quantities of positive and negative electricity must always be produced. Still this principle is also confirmed here, for from ordinary chlorine negative chlorine ions are formed only under such circumstances that, at the same time, the same number of positive ions is produced. The great activity of free chlorine in its action upon metals is conditioned by the great inclination of chlorine to pass over into the condition of ions; iodine, which presents this inclination in a far less degree, and has accordingly no such great *affinity to negative electricity*, if I may be allowed the expression, has correspondingly a far less capacity for transferring metals into the condition of ions, or, according to the customary but ill-chosen expression, to combine with them.

These considerations give us the explanation for the action which oxidizing agents show upon contact with platinum which is connected with the "nobler" metals. If we have, for example, gold in a solution of common salt, it has an

extremely slight tendency, if any at all, to form ions ; it is far removed from the possibility of taking from the sodium ions the necessary positive electricity. The entire action will then be limited to the gathering of a few chlorine ions upon the surface of the gold, and of a corresponding slight excess of sodium ions upon the platinum. But if now chlorine molecules be present, they find here opportunity to go over into negatively charged ions ; the corresponding quantity of positive electricity, which must be produced at the same time, passes through the platinum to the gold, and the latter is put in position to send out, or one may say is directly forced to send out, a corresponding number of positively charged atoms, or ions.

I wish to emphasize here that, without in any way altering the final result, the explanation may be also given somewhat differently. Instead of recognizing the direct cause of the action in the tendency of chlorine to form negative ions, the active role may be ascribed to the gold, and to it be referred a positive tendency, though slight yet at hand, to the formation of ions. Chlorine would then play the more passive role by opposing to its transfer into negative ions a very small resistance, which is overcome by the positive tendency of the gold. At present it may not be entirely easy to decide finally between these views ; yet, without a closer discussion of the question, for which, however, some material already is at hand, I believe that the preference is due to the first.

This presentation brings out under all circumstances the fact that the great significance which the positive ion of the electrolyte has in cases of metals of the character of zinc, completely disappears in this case of the nobler metals. In fact, under the given conditions, gold dissolves as well when sodium-chloride solution, as when hydrochloric acid, both saturated with chlorine, is present at the platinum, which proves that the positive ion present, which suffers no change at all by the action, is not concerned, but instead only the substance which is able to furnish negative ions. Weaker oxidizing agents, that is such with less tendency towards the formation of negative ions, as for example *bromine*, are ineffective, as I have convinced myself by making the experiment.

It is perhaps fitting, at this place, to say a few words in regard to the expressions "Tendency" and "Inclination," of which use has here been made. Expressions of this kind are properly looked upon in exact science as suspicious, so long as they are not accompanied by satisfying explanation in the form of a controllable definition. On the other hand, there manifests itself everywhere the need of expressions of this

kind for the representation of natural occurrences, and the cause thereof lies in the following.

The different forms of energy may be, as is known, always resolved into two factors, one of which possesses the property that, in a system with a definite kind of energy, a condition independent of the time may obtain only when this, which Helm calls the *intensity factor*, has the same value everywhere in the system. Conversely, anything happens in the system only under the condition that the values of this factor at two places thereof are different. Difference of the intensity-factor is therefore the cause that anything happens, and every difference of this kind represents a "Tendency" or "Inclination" of the system to equalize the difference. Now there are possibilities, as shall in another place be more fully explained, of hindering this equalization by the bringing to bear of appropriate, opposing intensity-differences of another form of energy; these are exactly the cases in which the above-mentioned expressions "Tendency" and "Inclination" clearly present themselves, because the action is ready to take place at any time when the hindrance present is removed. In this sense, that the system of metals, electrolytes, &c. at hand contains differences of intensity of chemical energy, which are compensated by corresponding opposing differences of electrical intensity, or of potential, and which assert themselves first when, by establishment of the electric conduction, the latter are made to vanish,—in this sense have *tendency* and *inclination* been used in the preceding, and, after this explanation, the further use of these terms may well appear permissible.

If we now turn back to the subject under consideration, we see that the dissolving of metals is in all cases in so far electric, as it depends upon the changing of the metals into (electrically charged) ions. The marked activity of the metals in the development of electric currents depends, on the one hand, upon their capacity to undergo this change, on the other upon their capacity of "metallic" conduction. Further, when currents cannot be developed because the necessary conductors are wanting, the quantity of energy corresponding to the change may assume the form of heat; as occurs, for example, with the dissolving of metals which do not separate hydrogen, such as copper, silver, bismuth, &c., in nitric acid or aqua regia. In this case the question is also one of the replacement, by metal ions, of the hydrogen ions present; but since the metal is not able to take the electricity necessary for the change directly from the hydrogen, a cause must be present to assist this action. Here, for example, the oxygen

of the nitric acid serves the purpose. As the latter is reduced to nitrous acid, a bivalent oxygen atom, that is one with two negative electrical charges, becomes free and, with two positive hydrogen ions, forms water. Thereby two metal ions with their corresponding positive charges can enter the liquid, or, in other words, are forced thereto by the excess of negative ions now contained in the liquid. The electricity remaining in the metal compensates the positive electricity, which, according to the general law of the "Conservation of Electricity," must be developed upon the separation of the negative oxygen atom. It can scarcely be necessary to add that all the quantities of electricity in question are, by Faraday's law, exactly equal to one another.

Finally, the question presents itself whether galvanic currents may not also be developed in aqueous solutions without the help of any metal, only by means of formation and destruction of ions. Let us consider a liquid which has the capacity of developing positive ions, and a second in contact with it which can create negative ions (or destroy positive ones); then the actions will again occur with especial readiness when care is taken that the corresponding quantities of electricity be conducted away. This is effected by the insertion of conductors of the first class, which are not chemically attacked, and which are connected so as to make possible a reciprocal neutralization of the displaced quantities of electricity.

This case becomes realized when we bring, for example, a solution of ferrous chloride in contact with one of sodium chloride containing free chlorine, and dip in both solutions connected electrodes of carbon or platinum. The bivalent ferrous ions in the ferrous chloride change into trivalent ferric ions. The negative quantity corresponding to the positive electricity is discharged through the electrode into the chlorine solution, and supplies there the amount of electricity necessary for the change of the molecular chlorine into chlorine ions, and this action continues until the supply of ferrous ions or chlorine molecules is exhausted.

It becomes at once clear that here we have again to do with a chemical "Action at a distance" of the above-described kind. For it plainly makes no difference as to the action whether the solutions of ferrous chloride and of chlorine are in immediate contact, or are separated from each other by any electrolyte, as for example sodium-chloride solution. For since the transfer of electricity takes place from and to the ions of the electrolytes, the ferric chloride is formed in this case not directly from the chlorine-water but at the submerged

platinum plate, and the chlorine seems consequently not to exert its action where it itself is located, but at any arbitrary distance. Since, under the customary views, this phenomenon presents a rather unusual aspect, I shall describe in a few words a suitable arrangement of the experiment.

The solutions in question are put into two small glass beakers; in one ferrous chloride, in the other a solution of sodium chloride saturated with chlorine: in the place of the latter a solution of bromine in common salt solution, or one of potassium bichromate and hydrochloric acid may be conveniently used. In each glass is placed a platinum electrode, and both these are joined by metallic connexion through a galvanometer. Finally the circuit is closed by an inverted siphon-tube filled with salt-solution, the ends of the tube being closed by parchment-paper. The galvanometer indicates at once a current which passes in the liquid from the ferrous chloride to the chlorine, and at the electrode in the ferrous chloride this salt changes into the ferric chloride. In order to render it evident that the action takes place neither at the parchment-paper nor uniformly in the entire liquid, but is limited to the surface of the electrode, where the formation of ferric ions from ferrous ions by the transfer of positive electricity is alone made possible, the ferrous-chloride solution (which is previously to be completely reduced by digestion with iron powder) may be treated with a little potassium sulphocyanate; the development of the red-brown coloration exclusively at the electrode becomes then readily apparent.

In place of ferrous chloride there may of course be employed any other "reducing" solution. In order to realize a case, where the transfer of electricity takes place without the intervention of metal ions, I have combined sodium bisulphite with a solution of sodium chloride containing bromine, and have observed entirely similar results; even when the connexion is made by a siphon filled with a solution of pure salt, in a few moments the presence of sulphuric acid may be detected by means of an acid solution of barium chloride, while at the same time sodium bromide, that is bromine ions, has been formed on the other side.

The change in the ions of the sulphite, which here takes place, may be explained in different ways. There exist in sodium bisulphite solution the negative ions HSO_3. The change of these into the more stable negative ions of sulphuric acid may be represented by the reaction

$$2HSO_3 + H_2O = H_2SO_3 + H_2SO_4,$$

in which the resulting acids may be considered as partially or

wholly dissociated. In order that this may become possible, both of the negative units of electricity of the HSO_3 ions must be removed; they pass through the electrode to the other solution, where they serve to change a bromine molecule, Br_2, into bromine ions. The same result is reached when the bivalent ions of the neutral sulphite, $\bar{S}\,O_3$, are supposed to be changed into sulphuric acid according to the reaction

$$\bar{S}O_3 + H_2O = H_2SO_4 :$$

for every molecular weight of sulphuric acid formed, two units (of 96540 coulombs each) of negative electricity must pass through the connecting wires.

The electromotive forces which are developed when different solutions act upon the same metal are not unknown; they were first extensively investigated by R. Arrott* and later by A. Wright and C. Thompson†. The possibility of analysing more closely the actions upon which they depend and of understanding these actions in this fundamental character, was first given by the consideration of the electrical relations of the ions, which indeed before Arrhenius developed his so extremely fruitful theory, was not carried out.

In conclusion I wish to add that the description of some of the experiments, which are communicated here, was completely worked out at my writing-table, *before I had seen anything of the phenomena in question*. After making the experiments on the following day, it was found that nothing in the description required to be altered. I do not mention this from feelings of pride, but in order to make clear the extraordinary ease and security with which the relations in question can be considered on the principles of Arrhenius's theory of free ions. Such facts speak more forcibly than any polemics for the value of this theory.

A number of interesting phenomena, with which I have met in further investigations on this chemical action at a distance, will be presented at another opportunity. I hope likewise, as soon as I can find the necessary time, to be able to produce some pertinent quantitative measurements. I do not mention this to keep others at present from the carrying out of such experiments and measurements, but, on the contrary, in order to express my conviction of the necessity of a searching quantitative study of this field.

University Laboratory of Physical Chemistry.
Leipsic, Germany, May 1891.

* Phil. Mag. [3] xxii. p. 427 (1843).
† Journ. Chem. Soc. 1887, p. 672.

XXIV. *Relation of Volta Electromotive Force to Latent Heat, Specific Gravity, &c. of Electrolytes.* By Dr. G. Gore, *F.R.S.**

IN a research "On Changes of Voltaic Energy of Alloys during Fusion" (Phil. Mag. *ante*, p. 27) I have shown that when an alloy of bismuth, lead, tin, and cadmium, and one of bismuth, lead, and tin, changed from the solid to the liquid state by gradual and uniform application of heat whilst immersed in a suitable electrolyte, it suddenly increased in electropositive state, showing that whilst absorbing latent heat it acquired greater electromotive force, and that when these alloys solidified, reverse effects occurred. M. J. Regnauld had previously shown (*Comptes Rendus Acad. Sci.* June 10, 1878; Chemical News, vol. xxxviii. p. 33) that liquid gallium was electropositive to solid gallium in a neutral solution of gallous sulphate.

In order to ascertain whether, in cases where the mere act of mixing or diluting electrolytes is known to be attended by absorption of heat, a similar increase of the power of exciting electromotive force occurs, I took the separate ingredients of a chilling-mixture, each in a liquid state and at the same atmospheric temperature, measured the electromotive force of a simple couple of cadmium and platinum † in each liquid separately by the null method of balance, with the aid of a suitable thermoelectric pile (see Proc. Birm. Phil. Soc. vol. iv. p. 130; The Electrician, 1884, vol. xii. p. 414), and a galvanometer, then mixed the liquids, immediately took the temperature of the mixture, and, after having allowed the liquid to acquire the atmospheric temperature, measured the electromotive force of the couple in it. As the changes of energy depend upon *each* of the ingredients of the mixture, it was necessary in each case to consider the alterations of the *mean* amount of electromotive force.

Distilled water was used in making all the solutions. The proportions of substances employed were in nearly all cases simple multiples of their equivalent weights. The thermometer employed in the first four experiments was graduated to ·2 of a Fahr. degree, and that used in all the other ones was capable of being read to ·01 of a Centigrade degree. The following are the particulars of the experiments:—

* Communicated by the Author.

† In experiments "Nos. 7 and 15" a zinc-platinum couple was used.

Experiment 1.

Saturated solution of Sulphate of Sodium + Dilute Sulphuric Acid.

		Fahr.
4 oz. by vol. of sat. sol. of Na_2SO_4	Temp. before mixing	55·6
„ „ 1 vol. H_2SO_4 + 19 vols. H_2O	„ after „	54·4
	Decrease	1·2 F. deg.

E.M.F. with Cd + Pt at 55°·6 Fahr.

	Volts.		Volts.
Sat. sol. of Na_2SO_4 =	·993	Calc. mean E.M.F. by vol. =	1·1388
Dilute H_2SO_4 . . . . =	1·28473		
The mixture		=	1·1789
			p.cent.
	Increase	·0401 =	3·51

The mean electromotive force had therefore increased whilst heat was being absorbed and rendered latent.

In all the remaining experiments the influence of dilution with water alone was examined.

Experiment 2.

823·5 grains of liquefied "glacial Acetic Acid" ($C_2H_4O_2$) + Water.

		Fahr.
50 c.c. of glacial acid	Temperature before mixing	57·8
21 „ water	„ after „	56·2
	Decrease	1·6 F. deg.

E.M.F. with Cd + Pt at 17° C.

	Volts.		Volts.
The glacial acid =	1·1074	Mean E.M.F. by weight =	1·0344
Water . . . . . =	·850		
The diluted acid		=	1·1074
			p.cent.
	Increase	·073 =	7·06

Experiment 3.

430 grains of Tartaric Acid in 310 grains of Water + Water.

		Fahr.
30 c.c. of the strong acid solution	Temp. before mixing . .	53·5
20 „ water	„ after „ . .	53·2
	Decrease	·3 F. deg.

E.M.F. with Cd + Pt at 61° Fahr.

	Volts.		Volts.
The concent. acid sol. =	1·1417	Mean E.M.F. by weight =	·9151
Water . . . . . =	·850		
The diluted acid		=	1·1074
			p.cent.
	Increase	·1923 =	21·0

The mean electromotive force had increased 21 per cent., notwithstanding that the amount of heat absorbed was relatively small, and that the water had nearly 24 per cent. less power of exciting electromotive force than the concentrated acid solution.

Experiment 4.

575 grains of Nitrate of Ammonium in 662 grains of Water + Water.

		Fahr.
44 centim. of sat. sol. of $AmNO_3$ / 34 „ water	Temp. before mixing	60·0
	„ after „	52·0
	Decrease	8·0 F. deg.

E.M.F. with Cd + Pt at 60° Fahr.

	Volts.		Volts.
Saturated sol. of $AmNO_3$	=·993	Mean E.M.F. by weight	=·9530
Water	=·850		
The diluted solution			=·9930
			p.cent.
		Increase	·0400=4·18

When two similar couples of cadmium platinum, one being in the concentrated and the other in the diluted solution, were opposed to each other with the galvanometer in the circuit, the one in the diluted liquid showed slightly the greater electromotive force; this was a much more delicate test. It is evident that notwithstanding the water had about fourteen per cent. less power than the saturated solution of exciting electromotive force, its addition to that liquid did not reduce the mean amount of that property.

In the remainder of the experiments a more sensitive thermometer capable of measuring ·01 of a Centigrade degree was employed.

Experiment 5.

Saturated solution of Nitrate of Sodium + Water.

		C.
500 grains $NaNO_3$ in 43 c.c. of water / 298 c.c. of water	Temp. before mixing	15·40
	„ after „	13·98
	Decrease	1·42 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volts		Volts
The saturated solution	=1·0073	Mean E.M.F. by weight	=·8816
Water	=·850		
The diluted solution			=1·0044
			p.cent.
		Increase	·1228=13·9

Experiment 6.

Saturated solution of Nitrate of Strontium + Water.

		C.
600 grains $Sr2NO_3$ in 63 c.c. of water	Temp. before mixing	15·52
164·5 c.c. of water	„ after „	14·44
	Decrease	1·08 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.
The saturated solution	=·9930	Mean E.M.F. by weight	=·9046
Water	=·850		
The diluted solution			=·9787
			p.cent.
		Increase	·0741=8·19

Experiment 7.

Solution of 40 grains of Chloride of Sodium in 40 c.c. of Water + 40 c.c. of Water.

I did not ascertain the change of temperature produced by dilution in this case. J. Thomsen and others had already shown by experiment that the dilution of an aqueous solution of chloride of sodium is attended by absorption of heat.

E.M.F. with Zn + Pt at 22° C.

	Volts.		Volts.
The strong solution	=1·2471	Mean E.M.F. by weight	=1·1889
Water	=1·1270		
The diluted solution			=1·2557
			p.cent.
		Increase	·0668=5·61

Experiment 8.

Strong solution of Sulphate of Sodium + Water.

		C.
142 grains Na_2SO_4 in 75·4 c.c. of water	Temp. before mixing	15·22
40·6 c.c. of water	„ after „	15·08
	Decrease	·14 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.
The strong solution	= ·993	Mean E.M.F. by weight	= ·9513
Water	= ·850		
The diluted solution			= ·9872
			p.cent.
		Increase	·0359=3·77

Experiment 9.

Strong solution of Sulphate of Ammonium + Water.

		C.
264 grns. Am_2SO_4 in 69·8 c.c. of water	Temp. before mixing	14·98
46 c.c. of water	„ after „	14·84
	Decrease	·14 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.
The strong solution	= ·9815	Mean E.M.F. by weight	= ·9356
Water	= ·850		
The diluted solution			= ·9758
			p.cent.
		Increase	·0402 = 4·30

Experiment 10.

Strong solution of Carbonate of Sodium + Water.

		C.
106 grns. Na_2CO_3 in 58 c.c. of water	Temp. before mixing =	12·70
58 c.c. of water	„ after „ =	12·42
	Decrease	·28 C. deg.

E.M.F. with Cd + Pt at 16° C.

	Volt.		Volt.
The strong solution	= ·7499	Mean E.M.F. by weight	= ·7972
Water	·850		
The diluted solution			= ·7527
			p.cent.
		Decrease	·0445 = 5·58

Experiment 11.

Strong solution of Nitrate of Potassium + Water.

		C.
200 grains of KNO_3 in 58 c.c. of water	Temp. before mixing	15·24
58 c.c. of water	„ after „	14·70
	Decrease	·54 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volts.		Volts.
The strong solution	= 1·0216	Mean E.M.F. by weight	= ·9443
Water	= ·850		
The diluted solution			= 1·01588
			p.cent.
		Increase	·07158 = 7·57

Experiment 12.

Strong solution of Chloride of Ammonium + Water.

		C.
400 grains AmCl in 86·5 c.c. of water	Temp. before mixing	14·80
129·6 c.c. of water	„ after „	14·61
	Decrease	·19 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.
The strong solution	= ·9358	Mean E.M.F. by weight	= ·8898
Water	= ·850		
The diluted solution			·92436
			p.cent.
		Increase	·0345 = 3·87

As in each of the foregoing twelve instances there was absorption of heat during the act of dilution, I now examined some cases in which dilution is known to be attended by evolution of heat. Care was taken to select those in which chemical action as usually understood did not operate.

Experiment 13.

272 grains of Hydrated Acetate of Sodium in Water + Water.

		C.
164 grains of the anhydrous salt in 39·5 c.c. of water	Temp. before mixing	16·30
155 c.c. of water	„ after „	16·44
	Increase	·14 C. deg.

E.M.F. with Cd + Pt at 20° C.

	Volt.		Volt.
The concentrated soln.	= ·9157	Mean E.M.F. by weight	= ·8712
Water	= ·850		
The diluted solution			= ·9072
			p.cent.
		Increase	·036 = 4·13

Experiment 14.

Strong solution of Sulphate of Magnesium in Water + Water.

		C.
240 grains of anhydrous $MgSO_4$ in 46 c.c. of water	Temp. before mixing	15·68
115 c.c. of water	„ after „	15·90
	Increase	·22 C. deg.

E.M.F. with Cd + Pt at 20°.

	Volt.		Volt.
The strong solution	= ·993	Mean E.M.F. by weight	= ·900
Water	= ·850		
The diluted solution			= ·9787
			p.cent.
		Increase	·0787 = 8·74

Experiment 15.

Concentrated solution of Chloride of Potassium + Water.

This case was selected from the curve of electromotive

force given in "Fig. 8" on page 489 of the Philosophical Magazine, Dec. 1890, as showing an increase of electromotive force on dilution.

		C.
20 grains of KCl in 20 c.c. of water / 180 c.c. of water	Temp. before mixing	14·50
	„ after „	14·54
	Increase	·04 C. deg.

E.M.F. with Zn + Pt at 21·5° C.

	Volts.		Volts.
The strong solution	= 1·1850	Mean E.M.F. by weight	= 1·1331
Water	= 1·1270		
The diluted solution			= 1·2550
			p. cent.
		Increase	·1219 = 10·75

The mean electromotive force had increased 10·75 per cent. notwithstanding that there was not only no absorption, but even a slight evolution and loss of heat during the act of dilution.

Experiment 16.

Saturated solution of Caustic Soda + Water.

		C.
600 grains of 90 per cent. Soda in 37 c.c. of water / 3844 c.c. of water	Temp. before mixing	15·74
	„ after „	23·85
	Increase	8·14 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.
The saturated solution	= ·9072	Mean E.M.F. by weight	= ·8602
Water	= ·850		
The diluted solution			= ·89004
			p.cent.
		Increase	·0298 = 3·46

Experiment 17.

50 c.c. of Concentrated Aqueous Hydrochloric Acid + Water.

		C.
655 grains of absolute HCl in 250 grains of H_2O / 381·5 c.c. of water	Temp. before mixing	14·12
	„ after „	16·52
	Increase	2·40 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volts.		Volts.
The concentrated acid	= 1·3362	Mean E.M.F. by weight	= ·9148
Water	= ·850		
The diluted acid			= 1·20.
			p. cent.
		Increase	·2869 = 31·39

Notwithstanding the loss of heat during dilution, the mean electromotive force had greatly increased. The electromotive force was quite variable in the acid solutions owing to their great degrees of strength and the evolution of gas.

Experiment 18.

Partly diluted Sulphuric Acid + Water.

The acid was sufficiently diluted to prevent the formation of a definite hydrate by chemical union.

		C.
30 c.c. of H_2SO_4 in 20 c.c. of water	Temp. before mixing	13·0
20 c.c. of water	„ after „	24·0
	Increase	11·0 C. deg.

E.M.F. with Cd + Pt at 15° C.

	Volts.		Volts.
The strong acid soln.	=1·2504	Mean E.M.F. by weight	=·9585
Water	=·850		
The diluted solution			=1·1960
			p. cent.
		Increase	=·2375=24·68

Notwithstanding the great loss of heat, there was a large increase of the mean amount of electromotive force.

Experiment 19.

Concentrated solution of Caustic Potash + Water.

		C.
377 grns. of KHO in 233 c.c. of water	Temp. before mixing	11·74
155·7 c.c. of water	„ after „	11·76
	Increase	·02 C. deg.

E.M.F. with Cd + Pt at 17° C.

	Volt.		Volt.
The concentrated soln.	=·8951	Mean E.M.F. by weight	=·8779
Water	=·850		
The diluted solution			=·8929
			p.cent.
		Increase	·0150=1·7

Experiment 20.

Diluted solution of Caustic Ammonia + Water.

		C.
94·7 grains AmHO in 97·9 c.c. of water	Temp. before mixing	13·46
62·8 c.c. of water	„ after „	13·56
	Decrease	·10 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.
The less diluted solution	= ·89004	Mean E.M.F. by weight	= ·8746
Water	= ·850		
The more diluted solution			= ·8786
			p.cent.
		Increase	·004 = ·45

The amounts of electromotive force in this case were variable.

The following table contains the chief results of the experiments:—

TABLE I.

Mixture.	Temperature.		Mean E.M.F.	
		Degrees.		
Solution of Na_2SO_4 + dilute H_2SO_4 ...	Decrease	1·2 Fahr.	Increase	·0401
Liquid Acetic Acid + Water	,,	1·6 ,,	,,	·073
Solution of Tartaric Acid + Water ...	,,	·3 ,,	,,	·1923
,, $AmNO_3$ + Water.....	,,	8·0 ,,	,,	·040
,, $NaNO_3$ + ,, ...	,,	1·42 C.	,,	·1228
,, $Sr2NO_3$ + ,, ...	,,	1·08 ,,	,,	·0741
,, NaCl + ,, ...	,,	?	,,	*·0668
,, Na_2SO_4 + ,, ...	,,	·14 ,,	,,	·0359
,, Am_2SO_4 + ,, ...	,,	·14 ,,	,,	·0402
,, Na_2CO_3 + ,, ...	,,	·28 ,,	Decrease	·0445
,, KNO_3 + ,, ...	,,	·54 ,,	Increase	·0715
,, AmCl + ,, ...	,,	·19 ,,	,,	·0345
,, NaAcetate + ,, ...	Increase	·14 ,,	,,	·0360
,, $MgSO_4$ + ,, ...	,,	·22 ,,	,,	·0787
,, KCl + ,, ...	,,	·04 ,,	,,	*·1219
,, NaHO + ,, ...	,,	7·14 ,,	,,	·0298
,, HCl + ,, ...	,,	2·38 ,,	,,	·2872
,, H_2SO_4 + ,, ...	,,	11·00 ,,	,,	·2375
,, KHO + ,, ...	,,	·02 ,,	,,	·0150
,, H_4N + ,, ...	,,	·10 ,,	,,	·004

The various cases of absorption and evolution of heat given in this table agree with those given by J. Thomsen in his thermochemical researches (see P. Muir's 'Elements of Thermal Chemistry,' Appendix v.).

An inspection of the results thus obtained shows, 1st, that in 19 cases out of 20 *diluting an electrolyte or mixing it with another increased the mean amount of electromotive force of the two liquids*; and 2nd, that in 12 instances out of the 20 there was a lowering of temperature and an absorption of heat, and in the remainder an evolution and loss of latent heat, during the act of mixing.

As in the whole of the 8 cases in which there was evolution and loss of heat there was an increase of mean amount of

* In these two cases a positive plate of zinc was used.

electromotive force, it was evident that this increase could not be due to absorption of energy in the form of heat. I therefore examined the phenomena in another manner, to ascertain whether they were related to changes of total volume and of mean specific gravity of the two liquids during the act of mixing.

Different investigators have shown that when a concentrated aqueous solution of an acid, a salt, or an alkali, is diluted with water, a contraction of the total volume of the two liquids and an increase of the mean amount of their specific gravities occur in nearly every case (see Watts's 'Dictionary of Chemistry,' 2nd Supp. pp. 596–604). Marignac, however, found an exception with a mixture of a solution of neutral sulphate of sodium and sulphuric acid: in this case "expansion always occurs" (*ibid.* p. 604); he further observed that contraction takes place on diluting solutions of hydrochloric acid, sulphuric acid, chloride of sodium, and sulphate of sodium (*ibid.* pp. 603, 604). J. Thomsen and others have also shown that when a solution of caustic soda, and of various other substances, is diluted, the total volume of the two liquids becomes less (*ibid.* pp. 597–600). And Nicol has obtained similar results by separately diluting aqueous solutions of potassium chloride, potassium nitrate, sodium chloride, and sodium nitrate (Phil. Mag. vol. xv. 1883, p. 97; Journ. Chem. Soc. 1883, vol. xliii., Trans. p. 136).

In order to ascertain whether contraction occurred in the whole of the remainder of the cases in which I had found an increased mean amount of electromotive force developed during the mixing, the following arrangement (see figure) was employed:—A is a glass tube about 12 inches high and $\frac{1}{2}$ an inch in diameter, with a perfectly fitting stopcock in the middle. The lower end of this tube was closed by a vulcanized rubber bung, and the upper end was fitted with a perforated bung surmounted by a tall glass tube of narrow bore open at both ends, and provided with a scale or index capable of sliding up or down. The stopcock and bungs were coated with grease, and the apparatus was proved to be perfectly water-tight. The entire portion of the apparatus below the index-scale was immersed side by side with a sensitive thermometer in a large vessel of water at about 16° C., in order to keep the apparatus at a sufficiently uniform

temperature during the short period of an experiment. The thermometer was capable of measuring to ·01 of a Centigrade degree.

The lower compartment of the large tube and the bore of the stopcock were perfectly filled with the lightest of the two liquids at exactly the proper temperature; if this lower space was not sufficiently large a glass bulb was previously fixed water-tight on the lower end of the tube. The upper compartment and a part of the narrow tube was now filled with the heavier liquid, and the apparatus immersed in the bath. When the whole had acquired the same temperature, the tap was slightly opened for an instant and closed again, the index adjusted to the level of the meniscus, the tap then fully opened, the apparatus occasionally inverted, the liquids allowed to mix, and the changes of total volume of the liquids and the temperatures noted at stated intervals of time until all change of volume ceased. The apparatus and method are suitable for making accurate measurements. The following are the results obtained:—

TABLE II.

Change of Volume of Electrolytes by Dilution.

Substance.	Solution.	Water.	Change of Volume.
		c.c.	
Acetic acid...	11·0 c.c. of concentd. Acid.	10·5	Contraction 1·66 per cent.
KHO	11·0 „ satd. solution.	10·5	„ ·93 „
Am_2SO_4	11·0 „ „ „	10·5	„ ·61 „
$Sr2NO_3$	11·0 „ „ „	10·5	„ ·58 „
$MgSO_4$	11·0 „ „ „	10·5	„ ·293 „
Na Acetate...	11·0 „ „ „	10·5	„ ·187 „
AmCl	11·0 „ „ „	36·0	„ ·12 „
AmHO	10·5 „ $\frac{1}{6}$ „ „	11·0	„ extremely small.
„	10·5 „ $\frac{1}{2}$ „ „	11·0	Expansion ·0587 per cent.

With the solution of aqueous ammonia, if sufficiently dilute, contraction occurred, but when strong, expansion took place; probably similar results would be obtained with dilute hydrocyanic acid. Some practical mechanical application of liquid expansion by mixture might perhaps be made to produce hydrostatic pressure.

The above results, together with those previously obtained by other investigators (see references already given), show that in 18 out of the 20 mixtures of liquids employed in this research, contraction of total volume of the two electrolytes occurred during the act of mixing. This large proportion of cases of contraction indicates the existence of a great number of instances of the same kind, and that probably nearly all

electrolytes increase in mean amount of their specific gravities during mixture or dilution; these statements agree with the usual views entertained on the subject.

By comparison of these results with those in Table I., and those of Table I. with one another, it appears, 1st, that increase of mean specific gravity of the two liquids during dilution or mixing occurs not only in cases in which heat is evolved and lost, but also in those in which heat is absorbed and becomes latent; 2nd, that increase of mean electromotive force of the two liquids also occurs not only in those cases in which heat is absorbed and becomes latent, but also in those in which it is set free. And 3rd, that in 17 cases out of 20 an increase of mean specific gravity of the two liquids was attended by an increase of the mean amount of their electromotive force. We may therefore conclude that *in cases of mere physical mixture, the changes of mean specific gravity and of mean electromotive force of electrolytes are probably related to each other* as concomitant effects of the same cause, change of molecular motion. From the known general relation of increase of specific gravity to decrease of specific heat, it further suggests the inference that in cases of simple dilution the mean electromotive force of electrolytes is related to their mean specific heat.

As in all such cases, each phenomenon, whether it be physical mixture, dilution, specific gravity, specific heat, latent heat, or electromotive force, involves the mutual action of two substances, it is essentially necessary in every case to ascertain the *mean* amount of change occurring in the two substances.

In a separate and more extensive research, not yet published, I have measured the losses and gains of electromotive force by means of different positive metals in different classes of mixtures of electrolytes, including cases of chemical union as well as of mere physical mixture.

XXV. *The Study of Transformers.*

By Prof. John Perry, *F.R.S.*, *D.Sc.**

[The following paper was written in February last, at a time when I had been compelled to listen to many discussions on the Transformer. It has been nearly forgotten till now; but I see that it ought to be published now, so that it may precede my paper read four days ago before the Physical Society on 'Mr. Blakesley's method of Measuring Power in Transformers."—26th May, 1891.]

I HAVE been engaged on quite other matters during the last few years, and thought a few weeks ago that I must be hopelessly in arrear concerning the subject of

* Communicated by the Author.

transformers. Every year I give to students in an "Applied Mathematics" class the old-fashioned formulæ concerning two or more circuits; my students have generally worked a few numerical examples on transformers, and we have then gone on to other subjects.

I venture now to think that I have lost almost nothing by remaining for so long ignorant of the vague but reckless statements made by writers of papers on this subject, and that students will gain something by coming back to the old-fashioned method of treating it.

I say, on the assumption of constancy of magnetic permeability, of no hysteresis, and no heating of either iron or copper by eddy currents, what are the laws of a transformer?

Let this be found out first.

On comparing the theoretic and experimental results, we shall be in a position—we have never yet placed ourselves in this position—to theorize on the effect of the new phenomena, and even this it will not be wise to do until we observe whether magnetic leakage will not account for some of the discrepancy.

If one gives numerical values to resistances, sizes of iron, numbers of windings, &c. it is quite easy—a matter of a few hours at most—to calculate everything about all the currents for a transformer with two, three, or more coils.

This year, instead of asking my students to work a few numerical exercises, I asked them to work out quite a number of exercises on a transformer with two coils, and I venture to think that the numbers given by them in the following Tables are of even more interest—just now—than experimental results. The tables give results that no experimenter could give. I have had some experience myself, and really I cannot say that I see my way, with any ordinary dynamometer, to distinguish between a lag of 175° and 180°; whereas in these tables the lag sometimes varies for no load and full load between 179°·940 and 179°·942. The graphical method of working cannot distinguish differences so small as these.

As for the trouble of working,—my students have much other home-work to do, and they do it, and yet one of them has brought me two complete tables worked out at home between Friday and Monday.

Let V be the primary voltage, C the primary current, R primary resistance, L the primary self-induction, C′ the secondary current, R′ the secondary resistance, L′ the secondary self-induction, and M the mutual induction. Let ρ be a non-inductive part of the resistance of the secondary, the part external to the transformer. Let V′ be the voltage

at the terminals of ρ. Let P be the average power given to the primary, and P′ that given out by the secondary. Then, taking

$$\left.\begin{aligned} V &= a\sin\frac{2\pi}{\tau}t, \\ C &= A\sin\left(\frac{2\pi}{\tau}t-\epsilon\right), \\ C' &= A'\sin\left(\frac{2\pi}{\tau}t-\epsilon'\right), \\ V' &= a'\sin\left(\frac{2\pi}{\tau}t-\epsilon'\right)=\rho C', \\ P &= \tfrac{1}{2}aA\cos\epsilon, \quad P'=\tfrac{1}{2}\rho A'^2, \\ \text{Percentage efficiency} &= 100\,\frac{P'}{P}=E, \text{ say,} \end{aligned}\right\} \quad . \quad . \quad . \quad (1)$$

it is known that to calculate all the necessary values, the simplest plan is to calculate the following magnitudes first :—

$$\left.\begin{aligned} I' &= \sqrt{R'^2+\frac{4\pi^2L'^2}{\tau^2}}, \quad r = R+\frac{4\pi}{\tau^2}\frac{M^2R'}{I'^2} \\ l &= L-\frac{4\pi^2}{\tau^2}\frac{M^2L'}{I'^2}, \quad i=\sqrt{r^2+\frac{4\pi^2l^2}{\tau^2}} \end{aligned}\right\}$$

Then

$$\left.\begin{aligned} A &= \frac{a}{i}, \quad \tan\epsilon=\frac{2\pi l}{\tau r}, \\ A' &= \frac{2\pi}{\tau}a\frac{M}{I'i}, \quad \tan\epsilon'=\frac{\tau}{2\pi}\cdot\frac{\frac{4\pi^2}{\tau^2}L'l-R'r}{L'r+R'l}. \end{aligned}\right\} \quad . \quad . \quad (2)$$

As an example of a transformer with which we have experimented electrically and arithmetically, take R=10 ohms, R′=·1+ρ, a=1000 volts, L=10 secohms, L′=·1 secohm, and take as is usual M=1 secohm. That is, assume no magnetic leakage. We have the following interesting results obtained by altering τ, beginning with a frequency of 160 per second and ending with the rather absurd case of τ= more than 6 seconds. It is to be observed that when I say in any case that $\frac{2\pi}{\tau}$=1000, or 100, I really mean that $\frac{2\pi}{\tau}$L=10000 or 1000 respectively. It will be observed that L, M, and L′ only enter into the calculations in combi-

nation with $\frac{2\pi}{\tau}$. Hence, instead of saying that my tables show the effect of diminishing frequency in a given transformer, I might say that they really show the effect of keeping frequency constant and diminishing the section or increasing the length of the iron magnetic circuit.

Thus, for example, the table for $\frac{2\pi}{\tau}=100$ may mean

$$\frac{2\pi}{\tau}=100 \text{ and } L=10,\ M=1,\ L'=\cdot1\ ;$$

but this table is correct for

$$\frac{2\pi}{\tau}=1000, \text{ and } L=1,\ M=\cdot1,\ L'=\cdot01.$$

I shall only assume, in fact, that in any table the ratios of L to M and L′ remain constant.

For the sake of beginners it is well to state that, using amperes, volts, and ohms, if P and S are the numbers of windings of the primary and secondary respectively ; if a is the cross section of the iron in square centimetres, and λ the average length of the complete iron magnetic circuit and μ the permeability (being about 1500 in ordinary transformer working), we may take it that

$$\left.\begin{aligned} L &= P^2\frac{a\mu}{\lambda}\frac{4\pi}{10},\\ L' &= S^2\frac{a\mu}{\lambda}\frac{4\pi}{10}, \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (3)$$

and if there were no magnetic leakage—that is, if all the field due to a primary current through every winding of the primary passed through every single winding of the secondary, then

$$M=\sqrt{LL'}, \quad \text{or } M=PS\frac{a\mu}{\lambda}\frac{4\pi}{10}.$$

If two or three tables be compared for which the values of $\frac{2\pi}{\tau}$ L differ even greatly, it will be noticed that A′, ϵ', ρ' are practically the same from the very smallest to the greatest loads. Also, except for small loads A, ϵ, P, and E, are practically the same. This is the more striking as the frequency is greater. Now this is really the same as saying that if the ratios of L, L′, and M remain constant, considerable changes

in their absolute values do not greatly affect the results ; that is, considerable changes in μ do not affect the results ; that is, even hysteresis need not be expected to greatly affect the results.

$$\frac{2\pi}{\tau} L = 10000.$$

ρ.	A.	A′.	ϵ.	ϵ'.	a'.	P.	P′.	E.
∞	·100	0	89°9	179°939	100	·085	0	0
99·9	·141	·999	44·97	179·939	99·82	50·06	49·85	99·59
49·9	·223	1·997	26·5	179·940	99·61	99·95	99·45	99·49
9·9	·996	9·913	0·05	179·940	99·14	497·8	486·4	97·70
4·9	1·963	19·61	0	179·941	96·08	981·7	942·3	95·98
0·9	9·09	90·95	0	179·947	81·85	4545	3722	81·70
0·4	16·67	166·6	0	179·952	66·6	8335	5551	66·61
0·1	33·33	333·3	0	179·961	33·3	16667	5555	33·33
0	50	500	0	179·971	0	25000	0	0

$$\frac{2\pi}{\tau} L = 4000.$$

ρ.	A.	A′.	ϵ.	ϵ'.	a'.	P.	P′.	E.
∞	·25	0	89°85	179°9857	100	·055	0	0
99·9	·269	·9965	68·05	179·8601	99·55	51·52	49·49	96·05
49·9	·320	1·996	51·20	179·8573	99·6	100·1	99·4	99·28
9·9	1·02	9·902	13·89	179·8584	98·03	495·2	484·2	97·77
4·9	1·976	19·61	7·03	179·8597	96·10	980·4	942·3	96·07
0·9	9·09	90·88	1·25	179·8967	81·8	4544	3717	81·79
0·4	16·66	166·7	0·69	180	66·67	8332	5554	66·51
0·1	33·33	333	0·19	179·9047	33·3	16667	5555	27·02
0	50	500	0·17	179·8713	0	25000	0	0

$$\frac{2\pi}{\tau} L = 2000.$$

ρ.	A.	A′.	ϵ.	ϵ'.	a'.	P.	P′.	E.
∞	·5	0	89°72	179°713	100	1·275	0	0
99·9	·5094	·999	78·30	179·714	99·8	52·09	49·94	95·88
49·9	·5373	1·995	67·90	179·714	99·55	101	99·33	98·33
9·9	1·107	9·896	26·27	179·716	97·97	496	485	97·68
4·9	2·019	19·59	13·75	179·719	96·09	980	940	95·90
0·9	9·108	90·96	2·60	179·723	81·86	4550	3724	81·91
0·4	16·674	166·67	0·20	179·761	66·66	8336	5554	66·64
0	49·997	499·97	0·15	179·857	0	24998	0	0

$$\frac{2\pi}{\tau} L = 1500.$$

ρ.	A.	A′.	ϵ.	ϵ'.	a'.	P.	P′.	E.
∞	·667	0	89°6	179°962	100	2·328	0	0
99·9	·673	·999	81·08	179·817	99 82	52·16	49·85	95·6
49·9	·695	1·995	72·92	179·782	99·56	102·1	99·33	97·5
9·9	1·199	9·97	33·30	179·623	98·70	501	492	98·2
4·9	2·066	19·60	18·06	179·617	96·85	982	951	97·8
0·9	9·105	90·88	3·45	179·538	81·79	4553	4130	90·9
0·4	16·67	166·5	1·55	179·667	66·6	8333	5554	66·5
0·1	33·34	333·4	0·55	179·779	33·34	16660	5555	33·3
0	50	500	0·183	179·809	0	25000	0	0

$$\frac{2\pi}{\tau} L = 1000.$$

ρ.	A.	A′.	ϵ.	ϵ'.	a'.	P.	P′.	E.
∞	·999	0	89°427	179°427	100	4·997	0	0
100	1·004	·998	83·725	179·427	99·82	54·93	49·82	90·7
50	1·018	1·993	78·133	179·428	99·65	104·7	99·33	94·9
10	1·393	9·806	44·717	179·433	98·06	495	481	97·1
5	2·159	19·23	25·48	179·438	96·15	966	925	95·7
4	2·57	23·81	21·73	179·441	95·24	1195	1133	94·85
3	3·27	31·25	16·67	179·445	93·75	1567	1464	93·47
2	4·64	45·44	11·31	179·453	90·88	2277	2065	90·73
1	8·383	83·32	5·75	179·475	83·32	4171	3470	83·25
0·5	14·3	142·8	2·94	179·509	71·39	7141	5097	71·39
0·1	33·34	333·3	0·77	179·618	33·33	16668	5556	33·33
0	50	500	0·29	179·714	0	25000	0	0

$$\frac{2\pi}{\tau} L = 500.$$

ρ.	A.	A′.	ϵ.	ϵ'.	a'.	P.	P′.	E.
∞	1·999	0	88°85	179°862	100	20·07	0	0
100	2·001	·998	85·98	178·887	99·79	70·06	49·8	71·1
50	2·006	1·992	83·57	178·833	99·58	111·9	99·2	88·65
10	2·234	9·914	62·53	178·845	99·14	515	491	95·4
5	2·519	17·66	49·1	178·877	95·30	825	780	96·74
1	8·531	83·33	11·35	178·95	83·33	4182	3471	83
0·5	14·39	139·2	5·83	178·99	69·6	6844	4679	68·3
0·1	33·37	333·4	1·52	179·24	33·34	16679	5557	33·45
0	50·08	500	0·58	179·43	0	25041	0	0

$$\frac{2\pi}{\tau} L = 250.$$

ρ.	A.	A′.	ϵ.	ϵ'.	a'.	P.	P′.	E.
			°	°				
∞	3·996	0	87·7	179·77	100	20·14	0	0
99·9	3·994	·999	86·25	177·712	99·82	130·7	49·85	38·1
49·9	3·996	1·997	84·85	177·713	99·65	179·2	99·5	55·5
9·9	4·078	9·893	73·7	177·731	95·83	572	484	84·6
4·9	4·381	19·6	61·18	177·767	95·04	1055	941	89·2
2·9	5·035	32·23	47·98	177·782	93·48	1686	1507	89·4
0·9	9·346	86·78	20·7	177·916	78·1	4371	3388	77·5
0·4	16·90	165·6	11·23	178·008	66·24	8287	5486	66·2
0·1	33·44	324·1	9·18	178·367	32·41	16500	5250	31·8
0	50	500	1·2	178·898	0	25000	0	0

$$\frac{2\pi}{\tau} L = 50.$$

ρ.	A.	A′.	ϵ.	ϵ'.	a'.	P.	P′.	E.
			°	°				
∞	19·6	0	79·69	168·69	100	1923	0	0
100	19·6	·98	78·42	168·70	97·85	1967	47·9	2·43
50	19·57	1·95	78·14	168·72	97·65	2011	95·4	4·74
10	19·45	9·62	75·97	168·80	96·15	2359	452	19·6
5	19·36	18·86	73·3	168·90	94·3	2778	890	32·03
4	19·31	23·36	72·81	168·94	93·44	2982	1092	36·6
3	19·27	30·68	69·87	169·03	92·04	3315	1412	42·6
2	19·28	44·65	65·8	169·19	89·30	3951	1994	50·5
1	19·81	82	55·17	169·61	82	5656	3359	59·38
0·5	21·99	141	40·47	170·27	70·4	8364	4957	59·25
0·1	35·58	330	14·21	172·41	33·0	17250	5457	31·64
0	50·74	498	5·6	174·29	0	25240	0	0

$$\frac{2\pi}{\tau} L = 10.$$

ρ.	A.	A′.	ϵ.	ϵ'.	a.	P.	P′.	E.
			°	°				
∞	70·7	0	45	174·269		25000	0	0
99·9	70·6	·706	45	135·033	70·53	24980	24·95	0·1
49·9	70·5	1·41	45	135·05	70·36	24970	49·61	0·2
9·9	70·4	7·04	44·75	135·3	69·7	24980	297·5	1·276
4·9	70·0	14·0	44·4	135·5	68·6	25010	480	1·92
0·9	67·6	67·6	42·0	135·7	60·8	25130	1634	6·5
0·4	65·0	130	38·7	139·98	52·0	25360	3380	13·3
0·1	62·1	282	29·7	146·3	28·2	26980	3976	14·74
0	50	357	14·01	143·8	0	24250	0	0

An examination of these Tables will suggest many experiments, and also will suggest simple general rules for all periodic currents.

It is to be observed that in the tables, 1000, A, A′, and a' divided by $\sqrt{2}$ give the readings on dynamometers of the primary voltage and primary current and secondary current and secondary voltage respectively, or their *effective* values.

Note that the lag ϵ varies considerably from no load to small ordinary loads, but the lag ϵ' is always nearly 180°. And hence the secondary voltage and currents are almost identically the same kind of function of time (only of opposite sign) as the primary voltage. To make this certain :—the general term in V, whatever V may be, may be written

$$a_i \sin ikt + b_i \cos ikt,$$

and the general term in v' is

$$\frac{a_i}{s} \sin (ikt - \pi) + \frac{b_i}{s} \cos (ikt - \pi),$$

where s is the same for all terms. We are here considering only the ith term.

Evidently this is

$$-\frac{a_i}{s} \sin ikt - \frac{b_i}{s} \cos ikt,$$

and it is to be noted also that the lag is more nearly 180° as i is greater. I have here used k to represent $\frac{2\pi}{\tau}$, the reciprocal of τ being the frequency. This is true also of the primary current when R′ is not great.

With these tables before us, certain generalizations may be made in the formulæ given above. I assume, as in the tables, no magnetic leakage, so that $M^2 = LL'$.

1st. When R′ is very great. Let $\frac{2\pi}{\tau}$ be written as k.

$$\left.\begin{aligned} &I' = R', \quad r = R + k^2 \frac{M^2}{R'}, \\ &l = L, \\ &i = \sqrt{\left(R + \frac{k^2 M^2}{R'}\right)^2 + k^2 L^2}, \\ &A = \frac{a}{\sqrt{\left(R + \frac{k^2 M^2}{R'}\right)^2 + k^2 L^2}}, \qquad \tan \epsilon = k \frac{LR'}{R'R \times k^2 M^2}, \\ &A' = k \frac{MA}{R'} = \frac{Ma}{R'L} \text{ nearly}, \\ &\tan \epsilon' = -k \cdot \frac{RR'}{L'R + R'L + \frac{k^2 M^2 L'}{R'}}, \text{ or } \epsilon' \text{ nearly } 180°. \end{aligned}\right\} \quad (4)$$

Of course, if $R'=\infty$, there is further simplification:

$$r=R,\ i=\sqrt{R^2+k^2L^2},\ A=\frac{a}{\sqrt{R^2+k^2L^2}}=\frac{a}{kL}\text{ nearly};$$

$$\tan\epsilon=\frac{kL}{R},\quad \therefore\ \epsilon=90^\circ\text{ very nearly},$$

$$A'=\frac{Ma}{R'L}=0,\quad \tan\epsilon'=-\frac{1}{k}\cdot\frac{R}{L}=-\frac{R}{Lk},$$

or ϵ' is nearly 180°.

Hence, if the periodic function is not merely a simple sine function; if R′ is very great, the primary current is a very different function of the time from the primary voltage, whereas the secondary current and secondary voltage are the same kinds of function of the time as the primary voltage.

2nd. When R′ very small:

$$\left.\begin{aligned} &I'=kL',\ l=0,\ r=R+\frac{M^2R'}{L'^2},\ i=R+\frac{L}{L'}R',\\ &\text{and}\\ &A=\frac{a}{R+\frac{L}{L'}R'},\quad \tan\epsilon=0,\\ &A'=\frac{aM}{L'R+LR'},\quad \tan\epsilon'=0, \end{aligned}\right\}\quad . \quad . \quad (5)$$

Hence, in general, whatever be the law of current, both the primary and secondary currents, and therefore the secondary voltage, are the same functions of the time as the primary voltage, and to calculate their dynamometer readings is very simple.

3rd. As a help to the memory, it may be remarked that the primary current is just what it would be if there were no secondary circuit and if the resistance and self-induction were r and l respectively.

When R′ is great, we have practically $r=R$ and $l=L$.

When R′ is small,

$$r=R+\frac{M^2R'}{L'^2}\quad\text{and}\quad l=\frac{LL'-M^2}{L'};\quad .\quad .\quad .\quad .\quad (6)$$

and as these do not involve the periodicity, we may say generally, whatever be the law of change of primary voltage in an ordinary transformer,

$$V=r\,C+l\dot{C},$$

using the above values for almost no loads and for great loads.

4th. If we imagine no magnetic leakage, $l=0$, and we have

$$C=\frac{V}{R+\frac{M^2}{L'^2}R'} \text{ or } =\frac{V}{R+\frac{P}{S}R'} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

for all kinds of current variation unless R′ is large.

5th. We see that, except when R′ is great, $A'=\frac{M}{L'}A$, and when R′ is infinity, $A'=0$, and $A=\frac{a}{KL}$; so that, except for a very small range of small loads, we might expect the law

$$A = \frac{a}{kL}+\frac{L'A'}{M}$$

to be nearly true.

This law is very easily tested by means of the Tables.

Having seen, then, from the Tables the small inaccuracies of such a law, we might expect that generally

$$\textit{Effective } C=m+n\times \text{effective } C_1, \quad . \quad . \quad . \quad . \quad (8)$$

where n is constant and nearly equal to $\frac{S}{P}$, however the frequency &c. may alter, but m is a small constant which alters if the frequency alters. We should expect this law to be true when the secondary circuit is open, and also when the secondary current changes from small loads to the very greatest loads, and when it is short-circuited; but for very small loads it is somewhat untrue. For all practical purposes it is true.

6th. As, unless when R′ is very great,

$$A'=\frac{aM}{R'L+RL'}=\frac{a\frac{S}{P}}{R'+R\frac{S^2}{P^2}}.$$

If $R'=R_0+\rho$, then

$$a'=a\frac{S}{P}\cdot\frac{\rho}{R_0+\rho+R\frac{S^2}{P^2}} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This is Dr. Hopkinson's rule for the drop in the secondary volts as the load increases, when the currents are sine functions of the time. An examination of my Tables will show

that this law is wonderfully true for all loads. From what I have already said, it is obviously the rule whatever function of the time the current may be, if it is rapidly alternating. That is,

$$\text{Effective Secondary Voltage} = \text{Effective Primary Voltage} \times \frac{\frac{S}{P}\rho}{R_0+\rho+R\frac{S^2}{P^2}}. \quad (10)$$

In practice it is found that the secondary voltage "drops" more rapidly than this law would indicate—a result which might have been expected, as we know that there always is leakage.

May 26th.—When the above paper was being prepared in February last, not for publication, but to be handed about among my students to connect the results of their calculations, I asked some of them to repeat their calculations on the assumption that there may be magnetic leakage. That is, taking the same values of all their coil quantities as before, assuming that there may be a little magnetic leakage. I did not expect very great differences from the old numbers, but to my astonishment there were very great differences.

Thus, taking $R=10$ ohms, $R'=\cdot1+\rho$, $a=1000$ volts, $L=15$ secohms, $L'=\cdot15$ secohm, two students have worked out what is the effect of magnetic leakage, 1st, when the frequency is 106 per second; 2nd, when the frequency is 10·6 per second. In the first case, two tables were calculated; in the second case, four.

No general mathematical expressions will show so forcibly the necessity for caution in neglecting leakage.

Frequency 106 per second. $M=1\cdot50$.
No magnetic leakage. (Mr. Eliott.)

ρ.	A.	A'.	ϵ.	ϵ'.	a'.	P.	P'.	E.
∞	·1000	0	89·9	179·9394	100	·0850	0	0
99·9	·1412	·9991	44·97	179·9395	99·82	50·06	49·85	99·59
49·9	·2232	1·9965	26·5	179·9395	99·61	99·95	99·45	99·49
9·9	·9556	9·913	0·05	179·9401	99·14	497·8	486·4	97·70
4·9	1·9630	19·61	0	179·9409	96·08	981·7	942·3	95·98
0·9	9·09	90·95	0	179·9468	81·85	4545	3722	81·70
0·4	16·67	166·6	0	179·9519	66·64	8335	5551	66·61
0·1	33·33	333·3	0	179·9610	33·33	16667	5554	33·33
0	50	500	0	179·9708	0	25000	0	0

Frequency 106. M = 1·48.
$1\frac{1}{3}$ per cent. magnetic leakage. (Mr. Eliott.)

ρ.	A.	A′.	ϵ.	ϵ'.	a'.	P.	P′.	E.
∞	·1000	0	89°9	179°939	98·67	·085	0	0
99·9	·1412	·9808	46·4	181·5	98·49	48·61	48·54	99·70
49·9	·2228	1·968	29·5	182·98	95·98	96·96	96·65	99·68
9·9	·9627	9·458	20·4	194·8	93·63	451·2	442·8	98·13
4·9	1·741	17·15	30·4	204·85	84·05	750·8	720·7	96·01
0·9	3·370	33·28	68·2	247·6	29·95	628·4	498·2	79·27
0·4	3·658	36·11	77·6	257·33	14·44	392·8	260·7	66·37
0·1	3·726	36·78	83·7	263·55	3·678	204·4	53·75	26·29
0	3·739	36·91	85·8	265·7	0	136·9	0	0

Frequency 10·6 per second. M = 1·50.
No magnetic leakage. (Mr. Howitt.)

ρ	A.	A′.	ϵ.	ϵ'.	a'.	P.	P′.	E.
∞	·9995	0	89°42707	179°42707	100	4·997	0	0
100	1·004	·9982	83·725	179·42764	99·82	54·93	49·815	90·7
50	1·018	1·993	78·133	179·428203	99·65	104·7	99·33	94·9
10	1·393	9·806	44·7166	179·43268	98·06	494·9	480·7	97·1
5	2·159	19·23	26·4833	179·43808	96·15	966·2	924·5	95·68
4	2·57	23·81	21·73	179·441	95·24	1195	1133	94·85
3	3·27	31·25	16·67	179·445	93·75	1567	1464	93·47
2	4·64	45·44	11·31	179·453	90·88	2277	2065	90·73
1	8·383	83·32	5·75	179·4748	83·32	4171	3470	83·25
0·5	14·3	142·78	2·9416	179·5089	71·39	7141	5097	71·39
0·1	33·34	333·33	·766	179·61803	33·33	16668	5556	33·33
0	50	500	·28646	179·71352	0	25000	0	0

Frequency 19·6 per second. M = 1·485.
Magnetic leakage 1 per cent. (Mr. Howitt.)

ρ.	A.	A′.	ϵ.	ϵ'	a'.	P.	P′.	E.
∞	·9995	0	89°427	179°427	99	4·977	0	0
100	1·004	·988	83·836	179·54	98·8	53·85	48·8	90·55
50	1·017	1·972	78·37	179·65	98·6	102·6	97·25	94·75
10	1·393	9·705	45·83	180·56	97·05	485·35	470·95	97·03
5	2·157	19·02	28·65	181·63	95·1	946	905	95·63
4	2·571	23·56	24·45	182·156	94·2	1170·5	1109·5	94·79
3	3·268	30·89	20·23	183·005	92·7	1533	1432	93·4
2	4·629	44·85	16·48	184·63	89·7	2219·5	2012	90·63
1	8·281	81·51	15·18	188·9	81·5	3997	3321·5	83·1
0·5	13·79	136·3	18·85	195·41	68·15	6525	4646	71·2
0·1	27·87	275·8	34·44	213·29	27·58	11490	3803·5	33·11
0	35·53	351·8	45·28	224·71	0	12500	0	0

Frequency 10·6 per second. M = 1·425.
Magnetic leakage 5 per cent. (Mr. Howitt.)

ρ.	A.	A′.	ϵ.	ϵ'.	α'.	P.	P′.	E.
			°	°				
∞	·9995	0	89·427	179·427	95	4·997	0	0
100	1·004	·948	84·268	179·985	94·8	50	44·94	89·8
50	1·017	1·892	79·253	180·54	94·6	94·9	89·55	94·35
10	1·389	9·279	50·18	184·9	92·8	444·5	430·6	96·86
5	2·101	17·99	37·097	190·07	89·9	847·5	808·5	95·42
4	2·512	22·08	34·83	192·54	88·3	1031	975	94·57
3	3·138	28·47	33·66	196·436	85·4	1305·5	1216	93·12
2	4·261	39·62	35·3	203·44	77·2	1738·5	1569·5	90·26
1	6·536	61·72	45·05	218·776	61·7	2308·5	1904·5	82·49
0·5	8·379	79·45	57·59	234·155	39·7	2245·5	1578·5	70·31
0·1	9·822	93·42	74·01	252·865	9·3	1353	436·3	32·17
0	10·06	95·54	78·97	258·4	0	962	0	0

Frequency 10·6 per second. M = 1·35.
Magnetic leakage 10 per cent. (Mr. Howitt.)

ρ.	A.	A′.	ϵ.	ϵ'.	α'.	P.	P′.	E.
			°	°				
∞	·9995	0	89·427	179·427	90	4·997	0	0
100	1·003	·8981	84·808	180·514	89·81	45·41	40·33	88·82
50	1·017	1·793	80·308	181·596	89·65	85·6	80·3	93·77
10	1·372	8·690	55·287	190·00	86·90	390·7	378	96·63
5	2·033	16·31	46·59	199·57	81·55	698·5	664·5	95·14
4	2·353	19·51	46·17	203·87	78·36	814·5	768	94·25
3	2·825	24·29	47·51	210·29	72·87	954	884·5	92·72
2	3·532	31·11	52·36	220·5	62·22	1078·5	968	89·73
1	4·494	40·22	63·85	237·57	40·22	990·5	808·5	81·64
0·5	4·962	44·57	73·01	249·71	22·28	719	496·6	69·07
0·1	5·205	46·84	82·02	261·02	4·68	354·8	109·7	30·91
0	5·237	47·13	84·56	263·99	0	248·2	0	0

To show the effect of even a magnetic leakage so small as *one-tenth of one per cent.* Let $y = ·001$, where

$$M = \sqrt{LL'}(1-y).$$

Taking, as before, $L = 15$, $L' = ·15$, $LL' - M^2 = 4·5\,y$,

$$I' = KL', \quad r = R + \frac{M^2 R'}{L'^2} = R + 100\,R' \text{ nearly},$$

$$l = L - \frac{M^2 L}{L'^2} = 30y = ·03.$$

Take $V = 1000 \sin kt$, where $k = 1000$, and therefore the frequency is 159, we have the following results :—

R′.	C if there is no magnetic leakage.	C if there is a leakage of one-tenth of one per cent.
1	9·0909 sin kt.	8·79 sin $(kt-15°)$.
·5	16·6667 sin kt.	14·907 sin $(kt-27°)$.
·2	33·333 sin kt.	23·57 sin $(kt-45°)$.
·1	50 sin kt.	27·74 sin $(kt-56°)$.

So that even when the leakage is so insignificant as this, its effect is very marked when there is a heavy load on the transformer. Of course, the secondary current and secondary voltage would exhibit the same kind of discrepance.

I do not know how much magnetic leakage there may be in an ordinary transformer ; and indeed my present purpose is only to show students that as there is always some leakage, it ought to be taken into consideration.

I think it impossible that the leakage should be less than one one-thousandth of the whole induction. That is, that ·001 of the whole induction produced by the primary escapes the secondary coil, and ·001 of the whole induction produced by the secondary escapes the primary. The result is practically the same as if I said that ·0005 of the primary escapes the secondary, and ·0015 of the secondary escapes the primary. Now, taking a current of frequency 159 with the above-mentioned transformer, let the primary voltage be

$$V=a_1\sin(1000\,t+\alpha_1)+a_2\sin(2000\,t+\alpha_2)+a_3\sin(3000t+\alpha_3)+a_4\sin(4000\,t+\alpha_4)+\text{ \&c.}$$

If there were no leakage, the primary current would be with great exactness, if R′=1 ohm,

$$C=\frac{a_1}{110}\sin(1000\,t+\alpha_1)+\frac{a_2}{110}\sin(2000\,t+\alpha_2)+\frac{a_3}{110}\sin(3000\,t+\alpha_3)+\frac{a_4}{110}\sin(4000\,t+\alpha_4)+\text{ \&c.}$$

Whereas with only one-tenth of one per cent. of leakage, the primary current is

$$C=\frac{a_1}{112\cdot7}\sin(1000\,t+\alpha_1-15°)+\frac{a_2}{125\cdot3}\sin(2000\,t+\alpha_2-28°\cdot6)+\frac{a_3}{142}\sin(3000\,t+\alpha_3-39°)+\frac{a_4}{163}\sin(4000\,t+\alpha_4-48°)+\text{ \&c.}$$

The higher harmonics diminishing more and more rapidly, and having greater and greater lag.

In the light of our general expressions (2), it will be seen in the third statement and (6) that $\frac{LL'-M^2}{L'}$ represents a resultant coefficient of self-induction in the primary coil, unless for exceedingly small loads, and the resistance is $R+\frac{M^2R'}{L'^2}$. Hence, unless the leakage is very small indeed, or very great, it is obvious that the primary current cannot be a periodic function of the same kind as the primary voltage. The Tables and expressions show that this is also the case with the secondary current. They also show that the secondary and primary currents are nearly the same functions of the time, although opposite in sign, and that they are nearly proportional to one another.

All necessary general rules suggested by the Tables are easily worked out from the formulæ. But the suggestions are such that it is evidently worth while to treat the subject more generally, and those who are interested in symbolic methods, as employed in linear differential equation work, may prefer to see the equations written as

$$V=(R+L\theta)C+M\theta C', \quad . \quad . \quad . \quad . \quad (11)$$

$$O=M\theta C+(R'+L'\theta)C', \quad . \quad . \quad . \quad . \quad (12)$$

rather than in the usual way. Hence

$$C'=\frac{-M\theta}{RR'+(RL'+R'L)\theta+(LL'-M^2)\theta^2}V, \quad . \quad (13)$$

$$C=\frac{(R'+L'\theta)}{RR'+(RL'+R'L)\theta+(LL'-M^2)\theta^2}V, \quad . \quad (14)$$

where θ stands for $\frac{d}{dt}$, and θ^2 for $\frac{d^2}{dt^2}$.

These values are true for all kinds of currents, and any two circuits, whether there is iron present or not. We know that on a transformer L and L′ are practically proportional to P^2 and S^2, and M is nearly $=\sqrt{LL'}$.

From (3) and (4) at every instant,

$$-C=\frac{R'+L'\theta}{M\theta}C'=\left(\frac{R'}{M\theta}+\frac{L'}{M}\right)C'. \quad . \quad . \quad . \quad (15)$$

This result is of course derivable at once from equation (2). If R′ is small,

$$-C=\frac{L'}{M}C';$$

and even when R′ is not small, for frequencies and sizes of iron usual in transformers, the term $\frac{R'}{M\theta}$ is insignificant. In fact, the term $\frac{R'C'}{M\theta}$ even when $R'=\infty$ is merely the small value of C when the secondary is open, being then $\frac{-V}{R+L\theta}$. We may say then that it is true for all practical purposes that Effective $C=m+n\times$Effective C', where n is nearly $\frac{L'}{M}$ or $\frac{S}{P}$, m being a small constant which depends upon frequency, &c.

If R′ is small, or the loads are the usual loads on transformers,

$$C'=\frac{-V}{\frac{RL'+R'L}{M}+\frac{LL'-M^2}{M}\theta}, \quad . \quad . \quad (16)$$

$$C=\frac{V}{R+R'\frac{L}{L'}+\frac{LL'-M^2}{L'}\theta}. \quad . \quad . \quad . \quad (17)$$

Generally, then, unless when there is a very small load on the transformer :—

The secondary current is the same as if the primary voltage acted in one circuit of resistance

$$\frac{RL'+R'L}{M} \text{ or } R\frac{S}{P}+R'\frac{P}{S},$$

and self-induction $\frac{LL'-M^2}{M}$, there being no other circuit; and the primary current is as if the primary voltage acted in one circuit of resistance,

$$R+R'\frac{L}{L'} \text{ or } R+R\,\frac{P^2}{S^2},$$

and self-induction $\frac{LL'-M^2}{L'}$. When R′ is ∞, of course C is as before, the current in a circuit of resistance R and self-induction L, V being the voltage and $C'=0$.

Writing $M=\sqrt{LL'}(1-y)$, y being small, we may write (16) as

$$-C'=\frac{V}{R\frac{S}{P}+R'\frac{P}{S}+2Ly\theta}.$$

If, then, we can neglect $2Ly\theta$, we have the law when there is no leakage (9). But when $2Ly\theta$ cannot be neglected, of course the effect of it is to make the secondary voltage fall off more quickly as the load increases than would be indicated by formula (9). This I find shown by such actual experimental results on transformers as I have at command.

As I have already said, when we assume no magnetic leakage, it is of no importance whether we assume that permeability is constant or not, or whether there is hysteresis or not; the results given by (2) have been shown to be practically correct for such frequencies and amounts of iron &c. as are usual in transformers.

But if there is leakage y, and if μ and therefore L varies from instant to instant during a cycle, it is certain that y will alter in an inverse way. Making, then, the very unnecessary assumption that there is hysteresis in a transformer, it is obvious that Ly will not vary very much during a cycle, and the results of calculation will not be very different from what they are on the assumption that μ is constant. I have elsewhere given reasons for assuming that there is really no hysteresis in transformer working.

Taking the sizes of iron and other dimensions of any working transformer, and using them for calculating such tables as I have given, it will be found that on calculating the true power P given to the primary coil and comparing it with W, if W is

Effective Primary Volts × Effective Primary Current,

then $\frac{P}{W}$ is nearly 1, even when the load is rather small, and may be said to be exactly 1 for ordinary and all greater loads, if there is no magnetic leakage. But if there is magnetic leakage, $\frac{P}{W}$ is, as before, much less than 1 for very small loads, getting greater with the load until for heavy loads it reaches a maximum value, and for very heavy loads diminishes again. But it is always less than 1, and is less and less at its maximum value as the current departs further from a simple sine function of the time. In Mr. Eliott's two tables,

$$\frac{P}{W} = \cos \epsilon,$$

and without magnetic leakage ϵ is 0 for nearly the whole range of load—that is:—If there is no magnetic leakage, the power given to the transformer is obtained by multiplying

effective primary volts by effective primary amperes. But when there is magnetic leakage, this rule is wrong. The ratio of $\frac{P}{W}$, for example, in the second table is never greater than cos 20°. Such experimental results as are at my command confirm my view that

Effective Primary Volts × Effective Primary Amperes

give a result always greater than the true power, even for very great loads; a result to be expected if there is considerable magnetic leakage.

XXVI. Mr. Blakesley's *Method of Measuring Power in Transformers.* *By* Prof. J. Perry, *F.R.S.**

MR. BLAKESLEY'S method of measuring the power given to the primary coil of a transformer becomes more important the more it is studied. Mr. Blakesley proved it to be correct if currents followed the simplest periodic law; if there was no magnetic leakage; if magnetic permeability was constant. Any person who has used Fourier's theorem knows that if Mr. Blakesley's rule is right for a sine function, it must be right for any periodic function whatsoever; as any periodic function may be expressed in sine functions, and each of these enters into the equations as if it were alone†.

* Communicated by the Physical Society: read May 22, 1891.

† This assertion was challenged in the discussion. Perhaps I ought to have explained myself more fully. At the time I happened to be working with Fourier's Series very much, and I lost sight of the fact that what was very evident to me might not be evident to others.

If $$x=\Sigma_1^\infty (a_i \sin ikt+b_i \cos ikt),$$

and $$y=\Sigma_1^\infty (\alpha_i \sin ikt+\beta_i \cos ikt),$$

where $k=\frac{2\pi}{\tau}$ and τ is the periodic time, then the average value of xy between the limits 0 and τ is

$$\tfrac{1}{2}\Sigma(a_i \alpha_i+b_i \beta_i),$$

and does not involve any term such as $a_i \alpha_r$ or $b_i \beta_r$; that is, into the expression for the average value each term of the Fourier's Series enters just as if there were no other terms. Nearly all practical Electrical Engineers are in the habit of ignoring calculations which assume that a current is a sine function of the time; they say that such calculations are useless because the current never is a true sine function of the time. I have here given one of many examples which might be given in which a proposition concerning any periodic function need only be proved for one of the Fourier terms of that function. And in all cases, the result of the study of a sine function is at once applicable to any periodic function whatsoever.

Prof. Ayrton and Mr. Taylor have proved the method to be correct for currents of any periodic law, the permeability varying in any way whatever. But they make the assumption that there is no magnetic leakage.

I believe that it was Dr. Hopkinson who, in his paper read before the Royal Society on March 10th, 1887, first departed from the old-fashioned way of treating mathematically the equations concerning currents in neighbouring coils, and he has been followed by everybody else who has written upon that subject since. Some writers of eminence have given, and incompletely, Hopkinson's investigation, evidently not having seen his paper. In my opinion the usual method is somewhat misleading. Assuming no eddy currents in the conducting part of a transformer, the equations written in the old-fashioned, and in what I venture to say is the only correct way, become

$$\left.\begin{aligned} V &= RC + L\dot{C} + M\dot{C}' \\ 0 &= R'C' + M\dot{C} + L'\dot{C}' \end{aligned}\right\} \quad \ldots\ldots\ (1)$$

Here V is the voltage at the terminals of the primary circuit, R its resistance, C its current, and L its coefficient of self-induction. R′ is the resistance of the whole secondary circuit, in which we assume no independent electromotive force; C′ is its current, L′ is its coefficient of self-induction, and M is the mutual induction between the two circuits. It may be well to state that, using amperes, volts, and ohms:—If P and S are the numbers of windings of the primary and secondary respectively; if a is the cross section of the iron in square centimetres, λ the average length of the complete iron magnetic circuit, and μ the permeability (being about 1500 in ordinary transformer working), we may take it that

$$L = P^2 \frac{a\mu}{\lambda} \frac{4\pi}{10},$$

$$L' = S^2 \frac{a\mu}{\lambda} \frac{4\pi}{10};$$

and if there were no magnetic leakage—that is, if all the field due to a primary current through every single winding of the primary passed through every single winding of the secondary, then $M = \sqrt{LL'}$, or

$$M = PS \frac{a\mu}{\lambda} \frac{4\pi}{10}.$$

But there is always some magnetic leakage, and it fills me with astonishment that so many investigators should assume that a little leakage makes no difference.

To get an idea of the importance of even a little leakage let us eliminate $\dot{C}_1$ from equations (1) and we have the result

$$V = RC - R'\frac{M}{L'}C' + \frac{LL' - M^2}{L'}\dot{C}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The usual assumption that if LL′ only differs by a very little from M^2 the error is unimportant, is seen to be inadmissible when we consider how great a value $\dot{C}$ sometimes may have in comparison with C or C′. Thus, for example, in a transformer with which I have had something to do experimentally, L=15, L′=0·15, R=10, and M is very nearly 1·5; so that (2) becomes

$$V = 10C + 10R'C' + \left(15 - \frac{M^2}{L'}\right)\dot{C}.$$

Now, to take the very simplest kind of periodic current, and the one for which the above wrong assumption is least wrong, and a frequency of 106 per second—writing, in fact,

$$C = A \sin 1000\,t,$$

we know that

$$\dot{C} = 1000\,A \cos 1000\,t.$$

So that, even if M differs only by 1 per cent. from what it has been assumed to be, that is, if there is only 1 per cent. of magnetic leakage, the neglected term $\left(15 - \frac{M^2}{L'}\right)\dot{C}$ becomes of the value

$$\left\{15 - \frac{(1{\cdot}485)^2}{{\cdot}15}\right\}\dot{C},$$

or $0{\cdot}3\,\dot{C}$, or $300A \cos 1000\,t$. In fact, the neglected term becomes thirty times as important as the important and certainly hitherto non-neglected term RC in the equation.

Now in no case is the current truly a sine function of the time, and any departure from this simplest kind of periodic current makes the error of which I speak much greater.*

* As an example, one of many worked out by my students at Finsbury during the last few years: taking the sizes of iron from a certain Mordey transformer which I have occasionally used; assuming permeability constant and no eddy currents in copper or iron; assuming currents to be true sine functions of the time. If V is voltage at terminals of primary, primary resistance 10 ohms, internal secondary resistance 0·1 ohm, outside resistance of secondary in ohms being called ρ; self-induction of primary 15 secohms, self-induction of secondary 0·15 secohm; assuming V in volts $= 1000 \sin \frac{2\pi}{\tau}t$, and taking frequency 106 or $\tau = 1 \div 106$ second, it is quite easy to calculate to any number of places of decimals

Of course, any self-induction in the outside part of the secondary circuit will produce the same effect as a leakage in the transformer itself.

The interesting fact to which I wish to draw the attention of members of the Society is this, that however great may be the magnetic leakage, Mr. Blakesley's method is still correct if magnetic permeability is assumed constant during a cycle. Multiplying equation (2) by C we have

$$VC = RC^2 - \rho \frac{M}{L'} CC' + \frac{LL' - M^2}{L'} CC' \quad . \quad . \quad . \quad (3)$$

Integrating for the whole periodic time and dividing by

---

that may be desired, the amplitudes and lags of the primary and secondary currents, and indeed all other magnitudes involved. The graphic method of working is evidently quite out of the question.

My students have for several years made calculations of this kind, obtaining tables of values for various frequencies and amounts of iron in the transformer, and they are exceedingly instructive. Until such tables are compared with actual experimental results, it seems to me that debates as to the effect of hysteresis consist merely of assertions having no physical basis.

For my present purpose I will give part of two tables calculated by Mr. Eliott, one of my students. Taking the above values :—

1st. If we assume that there is no magnetic leakage. In that case $M = \sqrt{LL'} = 1{\cdot}5$ secohms. Using this value of M we get table I.

2nd. If we assume that there is a little magnetic leakage, say one and one third per cent., or that $M = 1{\cdot}48$ secohms. Using this value of M we get Table II.

Now it is perfectly certain that there is some magnetic leakage, always; but it is rather difficult to say just how much there may be. I have here assumed in taking $M = 1{\cdot}48$ instead of $1{\cdot}50$ that $1\frac{1}{3}$ per cent. of the total induction due to the primary coils does not pass through the secondary coils, and that $1\frac{1}{3}$ per cent. of the total induction due to the secondary coils does not pass through the primary coils. This number has been taken at random.

The meanings of the letters used at the heads of the various columns are these :—

If

$$V = 1000 \sin \frac{2\pi}{\tau} t,$$

$$C = A \sin \left(\frac{2\pi}{\tau} t - \epsilon \right),$$

$$C' = A' \sin \left(\frac{2\pi}{\tau} t - \epsilon' \right),$$

$$V' = a' \sin \left(\frac{2\pi}{\tau} t - \epsilon' \right) = \rho C',$$

P = average power given to primary,
P′ = average power given out by secondary.
Percentage efficiency = 100P′/P.

Evidently V′ is the voltage at the terminals of the secondary circuit. Angles of lag are given in degrees.

this time—that is, taking the average value of every term in (3) it is to be observed that

$$\frac{1}{\tau}\int_{t}^{\tau+t} \dot{C}C \,.\, dt = \frac{1}{\tau}\int_{C_0}^{C_0} C \,.\, dC = 0,$$

if C_0 is the value of C at the beginning and end of the period; and hence, as $\frac{M}{L'} = \frac{P}{S}$ very nearly,

$$\text{Average } VC = \text{average } RC^2 - \text{average } r\frac{P}{S}CC_1.$$

If either C or C′ were the current in a non-inductive circuit, a great error would be introduced by endeavouring to measure the average product by the split dynamometer method; but there is no such error here.

Hence Mr. Blakesley's method is correct, however great may be the magnetic leakage. It must be remembered, however, that I have neglected eddy currents in the copper and iron; and I assume magnetic permeability to be constant *during*

Now at full loads on this transformer it is perfectly obvious that currents, lags, and powers are immensely altered by this small amount of leakage which I have introduced as possible. The currents are ten times as great, and the lags are utterly different from what they have been supposed to be.

TABLE I.—No Magnetic Leakage, or M=1·5.

ρ.	A.	A′.	ϵ.	ϵ'.	P.	P′.	Effic.	a'.
			°	°				
∞	0·1000	0	89·9	179·9394	·0850	0	0	100
99·9	0·1412	0·9991	44·97	179·9395	50·06	49·85	99·59	99·82
49·9	0·2232	1·9965	26·50	179·9395	99·95	99·45	99·49	99·61
9·9	0·9956	9·913	0·05	179·9401	497·8	486·4	97·70	99·14
4·9	1·963	19·61	0	179·9409	981·7	942·3	95·98	96·08
0·9	9·09	90·95	0	179·9468	4545	3722	81·70	81·85
0·4	16·67	166·6	0	179·9519	8335	5551	66·61	66·64
0·1	33·33	333·3	0	179·9610	16667	5554	33·33	33·33
0	50	500	0	179·9708	25000	0	0	0

TABLE II.—One and one-third per cent Magnetic Leakage, or M=1·48.

ρ.	A.	A′.	ϵ.	ϵ'.	P.	P′.	Effic.	a'.
		°	°	°				
∞	·1000		89·9	179·939	·085	0	0	100
99·9	·1412	0·9858	46·4	181·5	48·61	48·54	99·70	98·49
49·9	·2228	1·968	29·5	182·98	96·96	96·65	99·68	95·98
9·9	·9627	9·458	20·4	194·8	451·2	442·8	98·13	93·63
4·9	1·741	17·15	30·4	204·85	750·8	720·7	96·01	84·05
0·9	3·370	33·28	68·2	247·6	628·4	498·2	79·27	29·95
0·4	3·658	36·11	77·6	257·33	392·8	260·7	66·37	14·44
0·1	3·726	36·78	83·7	263·55	204·4	53·75	26·29	3·678
0	3·739	36·91	85·8	265·7	136·9	0	0	0

a cycle. If I had time, I could show that in alternating-current calculations there are other very important uses of the fact that $\int_t^{\tau+t} x\dot{x}\,.\,dt=0$, if x is any periodic function of the time.

Added May 23rd, 1891.

In the discussion of this paper it was obvious that I had not at sufficient length made known what I meant by magnetic "*leakage*." It was owing to this, no doubt, that my introduction of the idea of the importance of leakage was looked upon as academic merely. Again, my use of the symbols L, M, and L′ did not seem to be understood, nor what they had to do with a transformer. It is therefore necessary that I should say more fully, but not more definitely than in the paper, that as M is always less than $\sqrt{LL'}$ owing to magnetic leakage, I define leakage as the value of y where

$$M=(1-y)\sqrt{LL'}.$$

Hence, if $L=P^2\frac{4\pi}{10}\frac{a\mu}{\lambda}$ or P^2m, say, then $L'=S^2m$ and $M=PSm(1-y)$.

Again, the method of treatment to which I object is to state the equations as

$$V=RC+P\frac{dI}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$0=R'C'+S\frac{dI}{dt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

I affirm that the induction I of equation (1) is a very different thing from the I of equation (2). As the old Maxwell method of writing the equations does not seem to be understood, I wish to make it clear that if I did use the induction I would use I_p in equation (1) and I_s in equation (2), where

$$I_p=Pm(C+S)m(1-y)C',$$
$$I_s=Pm(1-y)C+SmC'.$$

This is assuming that the number of ampere-turns which produces the effective induction through the primary is $PC+SC'(1-y)$; and the number of ampere-turns which produces the effective induction through the secondary is

$$PC(1-y)+SC'.$$

In fact, as I stated clearly when reading the paper, y is the

fractional portion of the field due to primary current which escapes the secondary winding, or it is the fractional portion of the field due to the secondary current which escapes the primary winding. The reasoning is the same even if a small difference be supposed to exist between the y of the first and the y of the second equation; that is, if M is not the same in the two circuits. I submit that in the absence of any prior definition of "leakage" this is simple and reasonable. Dr. Sumpner's "leakage" is a very different thing. He said, let $I_p = I_s(1+x)$, then x is the magnetic leakage.

Of course, on any reasonable assumption of alterations in μ, the permeability of iron, or on the most reasonable assumption that μ really is constant during a quickly-performed cycle, Dr. Sumpner's x varies greatly during the cycle. I cannot give a physical meaning to x. My "leakage" y does not vary if μ is constant during a cycle, and I have given a perfectly definite physical meaning to it.

It may be well to add, here, why I think it reasonable to assume μ constant during a cycle.

1st. I have shown that if there is any leakage, the use of equations (1) and (2) is quite unreasonable.

2nd. If there is any leakage, it is impossible to treat the subject mathematically unless some assumption is made concerning μ.

3rd. It is quite certain that the law of variation of μ when the cycle is very slowly performed must be quite different from the law when the cycle is very quickly performed, as it always is in practice.

4th. The analogies between magnetic stress and strain and ordinary stress and strain in materials are well established. Now every material exhibits strain hysteresis when slowly loaded and unloaded, and exhibits no hysteresis whatever when the loading and unloading are very quickly performed. Even the most inelastic of materials will transmit a musical note unchanged. Hence for years I have taught my students to look upon magnetic hysteresis as very important when cycles are slowly performed and as unimportant when cycles are very quickly performed. Unless on this assumption, how is it that there is so little heating of the iron of a transformer by hysteresis even when transforming the largest amounts of energy; and such heating as there is must be partly due to eddy currents. I therefore maintain that μ constant during a cycle (and this means that my "leakage" is constant during a cycle) is the only reasonable assumption that can be made in the present state of our knowledge.

But even if this reasonable assumption of no hysteresis and

of the constancy of μ during a cycle be denied me, and if I must assume the possibility of its being wrong, still $\frac{LL'-M^2}{L'}$ must be more nearly constant than μ; for it is equal to $2Ly$. And if μ increases and therefore L increases, y will certainly diminish, and if L diminishes y will certainly increase.

XXVII. *The Theory of Magnetism and the Absurdity of Diamagnetic Polarity. By* J. Parker, *M.A., Fellow of St. John's College, Cambridge* *.

THE most unsatisfactory part of the theory of magnetism is that which refers to the so-called diamagnetic bodies. This part of the theory is so beset with absurdities and contradictions that it is necessary to examine it closely and to point out the true explanation of the behaviour of the so-called diamagnetic bodies before we can give the general theory.

I published a short and somewhat premature paper on diamagnetism in the Philosophical Magazine for May 1889. A few weeks afterwards my ideas on the subject had ripened into their present form; but I determined to publish no more about it until after the appearance of my book on 'Elementary Thermodynamics,' which I was then intending to write. Finding, however, that my book was not likely to be finished as soon as I had expected, I published a second short paper on diamagnetism in the Philosophical Magazine for July 1890, which I thought would be sufficient to explain my ideas until I could give the subject the attention it deserved.

My second paper on diamagnetism was criticised, as I have since found, by Dr. Lodge with a great display of rhetoric in the next number of the Philosophical Magazine; but I was then so occupied that I did not see or hear of the criticism until the following November. When I then came to read it, I did not find anything which required me to modify any of my ideas on the subject in the slightest degree, and I concluded that Dr. Lodge had misunderstood my paper.

It is now proposed to consider the subject carefully and completely, by which means, it is hoped, the disputed points will be settled to the satisfaction of everybody. In so doing, I shall endeavour to prevent all misconception by making my arguments as clear and simple as possible. For this reason I shall employ none but the simplest mathematics,

* Communicated by the Author.

and shall avoid unnecessary references to the physical theories of magnetism.

To begin, the property which distinguishes the so-called diamagnetic bodies (like bismuth and copper) from the other, or paramagnetic bodies (like iron), is shown by the following classical experiment. A small bar, A, of the substance to be experimented on, is hung by a thread between the poles, NS, of a powerful electromagnet and then the magnet is excited. If the bar A be one of the so-called diamagnetic substances, it will set its length at right angles to the line joining the two poles of the electromagnet, as shown in the second accompanying figure, which is supposed to be a view as seen by an eye looking from above. If, however, the bar A be one of the paramagnetic substances, it sets its length along the line joining the two poles of the electromagnet.

Fig. 1.

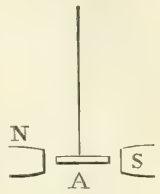
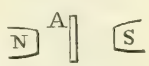


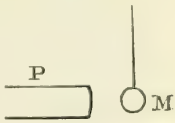
Fig. 2.



Instead of taking the above fundamental experiment as our starting-point, I prefer, for the sake of simplicity, to take another which is easier to understand. The second experiment has not yet been performed ; but it is admissible to make it the basis of our discussion, for not only is it equivalent to the classical experiment described above, but the inferences drawn from both will be the same.

In our ideal experiment, we take a powerful electromagnet whose poles are at a considerable distance apart, and hang a small piece, M, of the substance to be tested by a thread near either pole, P, of the electromagnet. Then on exciting the magnet, it is found that if M be a piece of iron, it is drawn nearer the pole P, while if it be a piece of bismuth, it would be driven further away from it.

Fig. 3.



The so-called explanation which is usually given of these phenomena may be divided into two parts :—

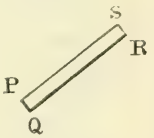
(*a*) It is supposed (that is, assumed) that the pressure of the air is strictly uniform all over the surface of M, from which it would follow that the pressure of the air can have no influence in causing the body M to approach or recede from the excited pole P.

(*b*) It is then supposed, as a necessary consequence, that when the electromagnet is excited, a piece of iron is attracted to the pole P, and that a piece of bismuth is repelled.

Experiments, which need not here be described, have been made with many solids and with liquids and gases, from which it is inferred that all substances are susceptible to magnetic influence, and it is supposed necessary to divide them into two classes: paramagnetic, those which, when placed near one pole of a magnet, are supposed to be attracted; diamagnetic, those which, under the same circumstances, are supposed to be repelled.

I first of all deny that (*a*) can be correct. For let an ideal right circular cylinder PQRS, indefinitely small in all its dimensions, be described in the air anywhere near the pole P of the electromagnet such that at no point within the cylinder is the magnetic force at right angles to the axis of the cylinder. Also let the ends PQ, RS of the cylinder be normal sections and suppose that the radius of each is indefinitely small in comparison with the length of the cylinder. Then since, in the state of equilibrium, the pressure of the magnetized air on any surface is evidently normal to that surface, just as if gravitation were the only action at a distance, it follows that the pressure of the air, per unit of area, at the end PQ of the cylinder is not the same as the pressure at the end RS. Thus in the space around the excited pole P, the pressure of the magnetized air varies from point to point, and therefore the assumption (*a*) cannot be correct.

Fig. 4.

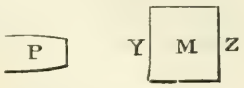


The explanations (*a*) and (*b*) must therefore be modified as follows :—It must be admitted that in the above experiment the pressure of the magnetized air is not quite uniform over the surface of M, but it may be supposed that the resultant pressure is so small in comparison with the action of the pole P that it is still necessary to divide bodies into two classes, viz. those which are attracted by the pole P, and those which are repelled by it.

Now if we recollect that the so-called diamagnetic bodies (like bismuth), which, when the magnet is excited, recede from the pole P, are caused to do so by a force which is evidently very minute, it will be easy to show that a very slight inequality (too small to be detected) in the pressure of the air on the surface of M is quite competent to produce the phenomena observed. Diamagnetic bodies may therefore be really attracted to the pole P, and only caused to recede from it by an excess in the pressure of the air on the side of M next to P over the pressure on the side remote from P; just as a balloon is attracted to the earth and only caused to ascend by the pressure of the air.

To make our argument simple, let us suppose that in our ideal experiment the body M is a cube each of whose edges is one centimetre, and let it be hung so symmetrically with respect to the magnet pole P that it is only on the face Y, next to P, and on the opposite face Z, that the pressure of the air need be considered. Also, for the sake of simplicity, let us suppose the pressure to be uniform over each of these faces. Then if the pressure of the air on the face Y exceed that on the face Z by the 1000th part of an atmo, the resultant pressure tending to drive M away from P will be rather over 1 gramme weight. If M be of bismuth, the most strongly pronounced of the so-called diamagnetic substances, the mass of the cube will be nearly 10 grammes. The resultant pressure of the air is therefore about $\frac{1}{10}$th of the weight of the cube. It will, therefore, be capable, in one second, of generating in the cube a velocity of 98 centimetres per second, and of causing it to move from rest through 49 centimetres. In $\frac{1}{4}$ of a second, it would generate in the cube a velocity of 24·5 centimetres (9·6 inches) per second, and cause it to move through 3 centimetres (1·2 inches). If the pressure on the face Y exceed that on the face Z by the 10,000th of an atmo, the resultant pressure tending to drive the cube away from P will be about the $\frac{1}{100}$th part of its weight. This would be sufficient, in one second, to give the cube a velocity of 9·8 centimetres (3·8 inches) per second, and to cause it to move through 4·9 centimetres. In $\frac{1}{2}$ second it would give the cube a velocity of 4·9 centimetres (1·9 inches) per second, and cause it to move through 1·2 centimetres (·46 inch).

Fig. 5.



The preceding calculations may well throw doubt on the common theory of diamagnetism, but the theory has still one apology left. It is found that diamagnetic bodies retain their characteristic property in a comparative "vacuum" of 2 or 3 millimetres of mercury (say the $\frac{1}{300}$th of an atmo). To explain this, we have only to observe that if, in our ideal experiment, the attraction of the pole P on the body M were strictly zero, the body M would be driven away from the excited pole P by the pressure of the air however good the "vacuum" might be, short of absolute perfection. Hence if the attraction of P on M be not strictly zero but exceedingly small, it will be necessary to reduce the density of the air very nearly to zero before this attraction can make itself manifest.

Having now shown that the common notion of diamagne-

tism rests on insufficient experimental evidence, or rather, on none at all, I may add that no one has ever attempted to support the notion by theory. This will prepare the way for my alternative idea, based on theory, that every substance placed near one pole of a magnet is attracted by the pole when the magnet is excited and can only be prevented from approaching the pole by some antagonistic cause, such as the pressures exerted by the contiguous objects. In the common theory of diamagnetism, it is supposed that bismuth is more powerfully repelled by a magnet pole than any other substance; according to my theory, bismuth is more feebly attracted than any other substance.

Before giving the theoretical grounds of the new theory, I cannot help observing that those who think the old theory of diamagnetism sufficient, should try to prove that the ascent of a balloon in the air is due to the diagravitational repulsion of the earth. Those who accept the new theory, will be content to regard diagravitation and diamagnetism as companion absurdities.

I was first led to reason theoretically on diamagnetism by reading the following remarkable article in Prof. Tait's 'Sketch of Thermodynamics':—"The commonly received opinion, that a diamagnetic body in a field of magnetic force takes the *opposite* polarity to that produced in a paramagnetic body similarly circumstanced, is thus attacked by Thomson by an application of the principle of energy. Since all paramagnetic bodies require time for the full development of their magnetism, and do not instantly lose it when the magnetizing force is removed, we may, of course, suppose the same to be true for diamagnetic bodies; and it is easy to see that in such a case a homogeneous non-crystalline diamagnetic sphere rotating in a field of magnetic force would, if it always tended to take the opposite distribution of magnetism to that acquired by iron under the same circumstances, be acted upon by a couple constantly tending to turn it in the same direction round its centre, and would therefore be a source of the perpetual motion."

This argument, which, for some unaccountable reason, seems to have been entirely neglected, requires to be slightly modified; for no notice is taken of the frictional resistance of the air to the rotation of the sphere, and it is not shown that the motion supposed to be thus derived in unlimited quantities may not be due to the absorption of heat at one temperature and its partial rejection at a lower. These defects may be obviated by supposing the sphere placed in a "perfect vacuum," and making provision to prevent the system

absorbing or giving out heat except at some constant absolute temperature θ. Also, for the sake of simplicity, we may suppose the sphere connected with mechanism, on which it does just so much work that its angular velocity of rotation remains constant. Under these conditions the system will assume an invariable state. If we then suppose that W is the mechanical work done on the system in any time, and Q the amount of heat absorbed, the principle of energy will give, since there is no change of state,

$$W+Q=0.$$

Now since work is obtained from the system, W is negative.
We see, therefore, that Q is positive.
But by Carnot's principle, we have

$$\frac{Q}{\theta}<0, \quad \text{or} \quad Q<0.$$

Thus Thomson's ideal experiment is inconsistent with both the principle of energy and with Carnot's principle, and the hypothesis of diamagnetic polarity is therefore disproved.

The argument adopted in the two papers I have published on diamagnetism in the Philosophical Magazine is only a modified form of Thomson's, but possesses the advantage of simplicity. It may be described thus: Take a piece of bismuth (or of any of the so-called diamagnetic substances) and place it within the action of a strong steel magnet whose poles are so far apart that only one of the poles, P say, exerts any sensible force on the bismuth. Then let the steel magnet be made immovable, and suppose the piece of bismuth held by a pair of pincers, or in some other way, so that it can either be kept at rest or moved about at will. Next, let the air be exhausted in the space about the bismuth until the "vacuum" is perfect, and, lastly, let means be taken to prevent the absorption or rejection of heat, except at some constant temperature θ.

If the piece of bismuth is held for some time in any position X and then suddenly moved to a new position Y, nearer to P, the magnetization of the bismuth will, of course, become ultimately stronger in the position Y than it was in the more remote position X; but, since magnetization requires time for its development, the change of position may be effected so rapidly that the magnetization of the bismuth has scarcely time to alter before the new position Y is reached. We thus see that the amount of mechanical work which can be obtained from the system of the steel magnet and the piece of bismuth during a given change of position depends,

among other things, on the speed at which the change of position is made. Suppose then, if possible, that the bismuth is repelled by the pole P, and let the system be made to undergo the following cycle of operations in two different ways :—

(1) When the piece of bismuth is in equilibrium in any position X at the uniform temperature θ, let it be moved to some other position Y, nearer P, so slowly that at every point of the path the bismuth is magnetized to the full extent and the temperature constant. The work done on the system in this operation will be positive, and may be written W.

Then let the piece of bismuth return slowly from Y to X by the previous path reversed. The whole of the work W will thus be returned by the system, so that, on the whole, there is neither loss nor gain of mechanical work during the cycle.

(2) Let the piece of bismuth be moved from X to Y so rapidly that the magnetization has scarcely time to change before the change of position is complete. The work that must be expended for this purpose is obviously $< W$; in fact, if the position X be far enough away from P, the work done on the system during the change of position may be practically zero. Next, let the piece of bismuth remain at rest in its new position until its magnetization has attained its permanent value. Then let it be brought rapidly back from Y to X by the first path reversed ; and, lastly, let it remain in the position X until the original state is attained. The mechanical work returned by the system in this way will be $> W$. Thus, on the whole, there is a gain of mechanical work during the cycle in which heat is absorbed and evolved at a constant temperature. This being impossible, by the principle of energy and Carnot's principle, we conclude that the assumption that the piece of bismuth is repelled by the pole of the magnet is absurd.

The foregoing cycle was described in my first paper on diamagnetism ; but the inference then drawn was, not that diamagnetism is impossible, but that Carnot's principle does not hold for diamagnetic bodies. In my second paper, I denied the existence of diamagnetism; but long before that time Duhem had arrived at the same conclusion, from reading my first paper, and had written a book on the subject.

I must now point out that Dr. Lodge has objected, with justice, to the preceding reasoning, that it contains a tacit assumption. Thus, even if we admit, as we are bound, that the magnetization of every body takes time to grow and to die away, it is not proved but that, in the second way of per-

forming the experiment described above, the assumed repulsive force between the steel and the bismuth may be so affected by the rapidity of the motion that the work required to force the bismuth from the position X to the position Y may be $> W$, and not less, as we supposed.

Dr. Lodge's objection may be illustrated very simply as follows :—Let a quantity of gas be contained in a cylinder fitted with a smooth air-tight piston, and suppose it to be provided that the cylinder can absorb or give out heat freely, but only at some constant temperature θ. When the whole is in equilibrium at the uniform temperature θ, let the piston be pushed in so slowly that the system is constantly in equilibrium, and the temperature always uniform and equal to θ. The work required for this purpose may be called W. Then let the piston be drawn out slowly until the original state is attained. The work restored will be W, and, on the whole, there will be neither loss nor gain of work.

Next, let the piston be pushed in as much as before, but far more rapidly. The work expended on the system in doing this will be $> W$. Now let the piston remain in its new position until the temperature has everywhere sunk to θ. Then let the piston be rapidly drawn out to its original place, and then wait until the original state is brought about. The work restored by the system will be $< W$, so that there will have been a loss of mechanical work in the cycle.

Dr. Lodge's objection may be obviated by means of two assumptions :—

(1) We assume that the magnetization of a body at rest may be in a state of unstable equilibrium. For example, in the experiment with the piece of bismuth, we assume that when the bismuth is at rest in any position X, the repulsive force of the steel magnet may have a value f which does not properly belong to the position X, and that this force may continue unchanged so long as the bismuth is held steadily enough in the position X. We further assume that if the bismuth be moved slowly from the position X, and then slowly brought back again, the repulsive force of the steel magnet will again be f, if sufficient care has been taken to move the bismuth about steadily. When the magnetization of a body at rest is in a state of unstable equilibrium, a slight shake, by which no perceptible amount of mechanical work is done, will be sufficient to cause the magnetization to rise or sink to its proper value.

(2) We also assume that if two magnetized bodies be moved about with any velocities, the attraction or repulsion between them when they are passing through any given

position may, if the experiment is made steadily enough, be exactly the same as if both bodies were at rest in that position with their magnetizations invariable.

In applying these assumptions to the second method of making the experiment with the piece of bismuth, let us suppose, merely for the sake of simplicity, that the magnetization of the steel is "rigid," that is, not merely unstably invariable, but invariable under all circumstances. Then let the cycle be performed as follows:—

(*a*) Let the bismuth be moved from X to Y so steadily that its magnetization is unaltered. It is evident that no thermal phenomenon will attend this operation, and that the work done on the system will be $< W$.

(*b*) The magnetization of the piece of bismuth now being in unstable equilibrium, let a slight shake, by which no perceptible amount of mechanical work is done, be given to the bismuth, in consequence of which the strength of the magnetization will be affected, and a thermal phenomenon take place. Then let the bismuth be held in the position Y until the temperature is again θ, and the magnetization at its proper value.

(*c*) Next let the piece of bismuth be brought back from Y to X by the first path reversed, and so steadily that the magnetization does not change. The work restored by the system during this operation is $> W$.

(*d*) Lastly, let a slight shake be given and hold the piece of bismuth in the position X until the system is in the original state.

We see therefore that if the two assumptions are made, the hypothesis of diamagnetism enables us to obtain work from a cycle in which heat can only be absorbed or given out at a given constant temperature θ. We now contend that the two assumptions are admissible. We shall establish the truth of this assertion indirectly by showing what results the two assumptions lead to when applied to several of the most important propositions in magnetism and electricity.

I. If in the modified Thomson's argument, we suppose the piece of bismuth replaced by any substance S which is attracted to the pole P, it will easily be seen that if the magnetization of S increases as the distance from P decreases, our two assumptions do not lead to a result in contradiction to the principle of energy and to Carnot's principle. We therefore conclude that a substance may be attracted by a magnet pole—a result which, of course, is in accordance with experiment.

It is necessary to notice another method of making the

experiment. If the substance S be brought from X to Y, a positive quantity of work, W_1 say, will be obtained. Then if S be turned round without altering the magnetization, the force between P and S will become repulsive, and therefore if S be brought back from Y to X without any change in the magnetization, another positive quantity of work, W_2 say, will be obtained. In this way, it might be thought, we could prove that S could not be attracted by P, but we must recollect that work will have been expended in turning S round. In fact, we may be sure that the work expended in turning S round, first in the position Y, and then in the position X, will be $> W_1 + W_2$.

II. Generally, if the substance M, when removed to a sufficient distance from the pole P, is in the neutral state, it can easily be proved that when M is near P, and its magnetization in stable equilibrium, M must be attracted by P with a force which increases as the distance from P decreases. Such a substance is defined to be "perfectly soft," and since unstable states of magnetization do not occur in practice, we may say that a "perfectly soft" substance can only be attracted by a magnet pole.

Of course, a substance S may be repelled by the pole P, but in that case, it can easily be shown, the magnetization of S could not be zero when it is at a great distance from P. The substance S would then be a permanent magnet, or its magnetization would consist of a permanent part combined with a temporary part induced by the influencing pole P.

III. If we now suppose the pole P replaced by a positively electrified body and the piece of bismuth by a negatively electrified body B, the force between the two bodies will be attractive, and when B is moved from X to Y in such a way that the distributions of the electrifications are in stable equilibrium, the attraction on B in the position Y will be greater than if the distributions had not been changed. Hence if W be the positive quantity of work yielded by the system when B is moved from X to Y in such a way that at every instant the distributions are in stable equilibrium, then when B is moved from its initial position X, in which the distributions are stable, to the second position Y, without any change in the distributions, the work yielded by the system will be $< W$. Also if, after causing the distributions in the position Y to become stable, we bring B back from X by the previous path reversed without any change in the distributions, the work so done on the system will be $> W$. Consequently, if the system is now caused to resume its original state, a complete cycle will have been undergone, and a posi-

tive quantity of work expended in it, which is in accordance with the principles of thermodynamics.

IV. Next, let both bodies be positively electrified, and suppose that they are at such a distance from one another throughout the experiment that the force between them is always repulsive. Then, when B is moved from X to Y in such a way that the distributions are constantly in stable equilibrium, the repulsion on B in the position Y will be less than if the distributions had not changed. (In the case of a supposed diamagnetic "soft substance," it will be recollected that the repulsive force in the position Y was greater than if there had been no change in the magnetization.) From this it is easily seen that electric repulsion is in accordance with the principles of thermodynamics.

V. Again, if we assume the principle of the conservation of electricity, which can be partially obtained as a theoretical deduction from the principle of energy and Carnot's principle, our two assumptions enable us to find expressions for the energy and entropy of an electrified system at rest in which the distribution of electricity is in equilibrium, stable or unstable. Then we can easily find the condition of electric stability on an insulated homogeneous conductor. For if P,Q be two points of such a conductor, our expressions show that if the potential have a higher value at P than at Q, it will be possible for electricity to pass, of itself, from P to Q, but not from Q to P. Conversely, if the potential at P be less than at Q, electricity will be able to pass, of itself, from Q to P, but not from P to Q. Suppose, for example, that the potential at P is greater than at Q: then a slight shake may cause a passage of electricity from P to Q, and this will diminish the potential at P and increase it at Q. Thus the potential tends to become uniform throughout the conductor, and when it has become uniform, the distribution is stable.

VI. Again, our expressions for the energy and entropy enable us to discuss the conditions of stability of two conductors A, B, separately homogeneous, which are in contact with each other, and isolated from all other bodies. For if P be a point in the body A, and Q a point in the body B, our expressions show that if the potential at P exceed the potential at Q by more than a certain amount, electricity will be able, of itself, to pass from P to Q, but not from Q to P; and conversely. Thus the condition of stability is that the potential should be uniform throughout each conductor, and that the two values should differ according to a certain law; all which is verified by experiment. Again, if the distributions be indefinitely near stable, and we suppose a small charge to pass from one conductor to the other, our theory indicates

that it will be necessary to impart or take away heat to keep the temperature of the junction of the two bodies constant. In other words, the theory gives both the difference of potential and the Peltier effect.

Now it is important to remark that by merely assuming our expressions for the energy and entropy to hold for stable distributions and without making any further use of the conception of unstable distributions, we can easily obtain the very same expressions for the difference of potential and the Peltier effect as before.

In like manner, we have two methods of discussing the question of a difference of potential and the law of the Thomson effect, in the case of two unequally heated portions of the same substance in contact, and both methods give the same results.

VII. Lastly, we have two ways of investigating Helmholtz's theory of the galvanic battery, and both lead to the same conclusions. This theory, it is true, has been questioned; but the objections appear to rest on misconceptions; and, besides, the theory does not seem to have been yet sufficiently explained. However, I do not propose to consider the subject any further at present, but merely wish to point out that we have two ways of getting the same result.

I have now, I consider, conclusively shown that my two assumptions are legitimate; and yet, at the same time, I acknowledge the importance of Dr. Lodge's objection, in requiring us to examine the tacit assumptions which lie at the root of all thermodynamical investigations of electricity and magnetism.

To conclude our discussion on diamagnetism, I observe that, so far as I am aware, no one has ever attempted to advance any serious theoretical or other arguments in favour of the common notion of diamagnetism. The theory appears to have owed its origin to the want of a theoretical examination of the subject, and to have been maintained from an excusable veneration for an old theory and a belief in the infallibility of the older scientists. Yet it has been occasionally questioned from the first. Duhem, in his book on diamagnetic bodies, mentions Becquerel and Plücker as having objected to the theory. Even in England there are persons who have never accepted it, and Dr. Lodge himself seems to be aware that it will not stand examination; for in his criticism on my two previous papers on the subject, he appears to rely chiefly on the strength of his rhetoric, and on an appeal to the name of Faraday.

I now proceed to the next part of the paper.

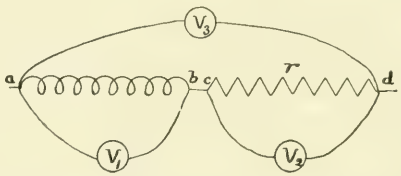
[To be continued.]

XXVIII. *Alternate Current and Potential Difference Analogies in the Methods of Measuring Power.* *By* Prof. W. E. Ayrton, *F.R.S.*, *and* W. E. Sumpner, *D.Sc.**

I.

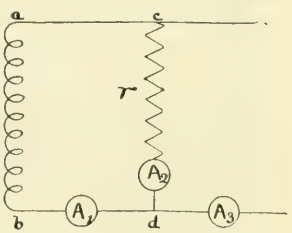
In a paper read by us before this Society on March 6th it was pointed out that for every problem involving alternate *P.Ds. in series* there was an analogous problem involving alternate *currents in parallel*. This general proposition tells us that we can transform each of the P.D. equations given, for example, in our paper on "The Measurement of the Power given by any Electric Current to any Circuit," read before the Royal Society, April 9th, 1891, into a current equation, and so transform our method of calculating power by the measurement of three P.Ds. into a method of calculating power by the measurement of three currents.

Fig. 1.



Such a transformation of our equations has been recently carried out by Dr. Fleming in the 'Electrician,' for May 8th, and the method he arrives at as well as the three-voltmeter method of which it is an analogue are seen in figures 2 and 1. If V_1, V_2, V_3 be the readings of the voltmeters in figure 1, and A_1, A_2, A_3 the readings of the three ammeters in figure 2, and r the resistance of the non-inductive portion of the circuit cd in each case, then the mean watts given to ab are respectively, whatever be the nature of the circuit ab, or of the current

Fig. 2.



$$\frac{1}{2r}(V_3^2 - V_1^2 - V_2^2)$$

and

$$\frac{r}{2}(A_3^2 - A_1^2 - A_2^2).$$

* Communicated by the Physical Society: read June 12, 1891.

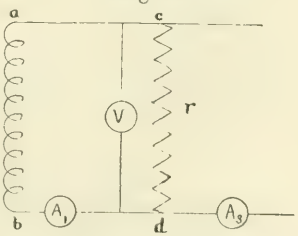
The three-ammeter method has the advantage over the three-voltmeter method, in that the dynamo need not give a larger P.D. than that necessary to send the current through *ab*; it is inferior to the three-voltmeter method in that while it is possible to measure V_1, V_2, and V_3 rapidly in succession by using only one voltmeter, it is, of course, impossible to use only one ammeter to measure A_1, A_2, and A_3 without constantly interrupting the circuit, and hence it would be necessary to accurately calibrate three instruments if this current method were employed.

But the main objection to this current method is that, as Dr. Fleming points out, it does not possess the accuracy of our three-voltmeter method of measuring power. For in order that this three-current method may give accurate results it is necessary to assume, to quote from our Royal Society paper, "the entire absence of self and mutual induction from a circuit some portion of which is necessarily of a solenoidal form."

It is possible, however, to obtain a current analogue of our three-voltmeter method which shall have the accuracy of the three-voltmeter method itself. And as the general proposition given in our previous paper tells us that the current analogues of P.D. arrangements *in series* are current arrangements *in parallel*, it follows that with this other method also the dynamo will not be required to produce a greater P.D. than that necessary to send the current through the circuit the power given to which we desire to measure.

The method is as follows:—In parallel with the circuit *ab* (fig. 3) the power given to which we wish to measure connect a non-inductive resistance of r ohms (in circuit with which no instrument is placed, which would necessarily make the so-called non-inductive branch more or less inductive). Let A_3, A_1, and V be the readings of the two ammeters and the voltmeter placed as shown, then, from the equations given in our Royal Society paper, it follows at once that the mean watts given to *ab* are

Fig. 3.



$$\frac{r}{2}\left\{A_3^2 - A_1^2 - \left(\frac{V}{r}\right)^2\right\}.$$

It is interesting to notice that if *ab* were the primary coil of a transformer, it would be when the load on the secondary

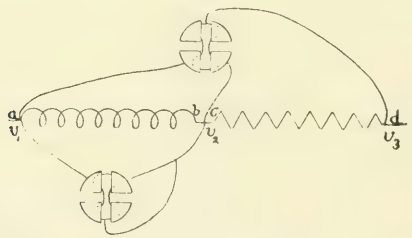
was small, that is when the current passing through *ab* was small, that it would be most difficult, on account of lag, to measure with ordinary methods the power given to *ab*. But that is exactly the case when it is most easy to use our one-voltmeter and two-ammeter method, since when the dynamo has to send little current through *ab* there is little objection to requiring it to send a current through *cd* in parallel with *ab*.

If the voltmeter (fig. 3) be a hot wire instrument, then, since an appreciable current will pass through this voltmeter, r must be taken as the parallel resistance of *cd* and of the voltmeter. It is important to observe, however, that there is no necessity to know either of these resistances separately, since the value of r can be determined when the three instruments A_1, A_3, and V are relatively calibrated thus :—First, break the circuits of *cd* and of the voltmeter, and compare the deflexion of A_3 with A_1; this calibrates ammeter A_3 relatively to ammeter A_1, the calibration of which we will assume to be correct ; second, close the circuits of *cd* and of the voltmeter, but break the transformer circuit *ab*, A_3 is now in series with the parallel circuit containing *cd* and the voltmeter. The value of r is therefore at once known, since r must equal the volts as read by V divided by the amperes as read by A_3.

II.

As an illustration of the general proposition to which we have referred, it may interest the Members to see what are the other analogies that we have traced out between alternate P.Ds. in series and alternate currents in parallel in connexion with the measurement of power.

Fig. 4.



Mr. Blakesley's method, communicated to this Society in February of this year *, is the current analogue of our electrometer method of 1881. For with the electrometer method (fig. 4) we make two measurements, one giving us the mean

* Phil. Mag. April 1891, p. 346.

value of

$$(v_1 - v_2)\left(v_3 - \frac{v_1 + v_2}{2}\right),$$

the other the mean value of

$$\frac{(v_1 - v_2)^2}{2},$$

v_1, v_2, v_3 being the instantaneous values of the potentials. Then we take the difference, and so get the mean value of

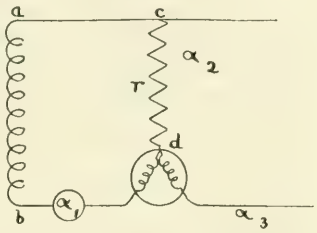
$$(v_1 - v_2)(v_2 - v_3),$$

which is equal to r times the mean watts given to ab (fig. 4).

With Mr. Blakesley's method two measurements are made, one with a split dynamometer (fig. 5) giving the mean value of

$$\alpha_1\alpha_3,$$

Fig. 5.



and the other with an ammeter giving the mean value of

$$\alpha_1^2,$$

α_1, α_2, α_3 being the instantaneous values of the currents. Then the difference is taken, and so the mean value of

$$\alpha_1(\alpha_3 - \alpha_1) \text{ or } \alpha_1\alpha_2$$

is obtained, and this is equal to $\frac{1}{r}$ times the mean watts given to ab (fig. 5).

It is important to notice that as no instrument is inserted in the non-inductive circuit ab (fig. 5), this method of Mr. Blakesley's has exactly the same accuracy as the electrometer method.

III.

The electrometer measurements may, as we pointed out some years ago, be varied; and by making the connexions as seen in fig. 6, we can obtain from the two readings the mean values of

$$(v_2 - v_3)\left(v_1 - \frac{v_2 + v_3}{2}\right)$$

and

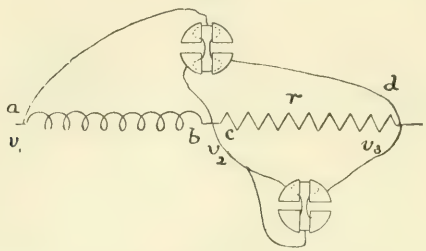
$$\frac{(v_2 - v_3)^2}{2};$$

then, taking the difference, we get the mean value of

$$(v_2-v_3)(v_1-v_2),$$

which, as before, is equal to r times the mean watts given to *ab*.

Fig. 6.



Mr. Blakesley has also pointed out, in his paper published in the Phil. Mag. for April of this year, that the current measurements may be varied and the apparatus arranged as seen in fig. 7. The two measurements now give respectively the mean values of

$$\alpha_2\alpha_3$$

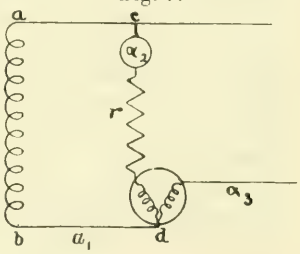
and

$$\alpha_2^{\,2};$$

therefore the difference gives the mean value of

$$\alpha_2(\alpha_3-\alpha_2),$$

Fig. 7.



that is, the mean value of

$$\alpha_2\alpha_1,$$

which is equal to $\frac{1}{r}$ times the mean watts given to *ab*.

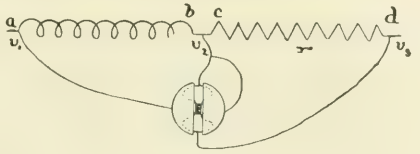
While, however, our second method of using the electrometer (fig. 6) gives the answer with the same accuracy as the first method (fig. 4), Mr. Blakesley's second method of joining up the dynamometers in figure 7 introduces self-induction into a circuit which ought to be entirely non-inductive, and so it does not give the answer with the same accuracy as his first method (fig. 5).

IV.

The modification of our electrometer method suggested to one of us by Mr. L. Atkinson, while he was a pupil at the Finsbury Technical College, and afterwards carried out by

MM. Blondlot and Curie, of making an electrometer with two needles for the measurement of power, is the exact analogue of the wattmeter method. For with the double-needle electrometer (fig. 8) we obtain from a single reading

Fig. 8.

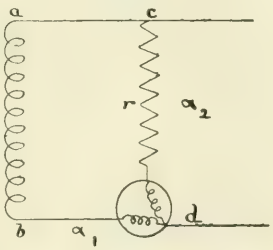


the mean value of

$$(v_1-v_2)(v_2-v_3),$$

which is equal to r into the mean watts given to *ab*. Similarly with the wattmeter (fig. 9) we obtain from a single reading the mean value of

Fig. 9.



$$\alpha_1\alpha_3,$$

which is proportional to $\frac{1}{r}$ into the mean watts given to *ab*.

While, however, the double-needle electrometer gives us the answer with perfect accuracy, the wattmeter method is liable to inaccuracy from the circuit *cd* not being strictly non-inductive.

Some years ago, at a meeting of the Institution of Electrical Engineers, one of us published the formula for the error made in using a wattmeter to measure the power given by an alternate current to an inductive circuit. Not wishing to cumber the pages of scientific periodicals with elementary mathematics, it was thought sufficient merely to state this formula without publishing a proof. But as our formula has now been introduced into text-books, and as the appropriation thereof by the writer of a well-known treatise has led him to supply a proof of it involving an appalling array of mathematical equations, we venture to offer a proof which, although very simple, is perfectly accurate. We are the more induced to do this because we find that this formula, and its proof for the error due to self-induction in the supposed non-inductive portion of the circuit *cd*, apply equally well to all the nine methods of measuring power illustrated in figures 1 to 9 of this paper.

The formula employed with such methods for giving the mean watts, whether it involves the reading of one instrument, as in the case of the wattmeter (fig. 9), or of two instruments, as with the methods illustrated in figures 4, 5, 6, 7, and 8, or of three instruments, as with the methods illustrated in figures 1, 2, and 3, gives with perfect accuracy r times the mean product of two currents, or $\frac{1}{r}$ times the mean product of two P.D.s. Whether this mean product is directly proportional to the mean watts given to *ab* depends in all the nine cases on the following consideration :—

The mean product between two currents which are sine functions of the time is, as every student now knows, equal to half the product of their maximum values into the cosine of the phase angle between them. Therefore if the angle of lag between the current in *ab* and the P.D. between its terminals be θ, and the angle of lag between the current in *cd* and the P.D. between its terminals be ϕ, and if the maximum values of the currents in these two circuits be A_1' and A_2' respectively, and the maximum values of the P.D.s at the terminals of these circuits be V_1' and V_2', it follows that the formula used to measure the watts in the cases 2, 3, 5, 7, and 9 gives

$$r\frac{A_1'A_2'\cos(\theta-\phi)}{2},$$

and in the cases 1, 4, 6, and 8,

$$\frac{V_1'V_2'\cos(\theta-\phi)}{2r}.$$

But what we want to measure is the mean product of the current in *ab* into the P.D. between its terminals, and this product equals

$$\frac{A_1'V_1'\cos\theta}{2}.$$

But

$$rA_2'=V_2'\cos\phi;$$

and in the methods illustrated in the figures 2, 3, 5, 7, and 9

$$V_2'=V_1',$$

while in the methods illustrated in the figures 1, 4, 6, and 8

$$A_2'=A_1';$$

therefore in all the nine cases

$$\frac{\text{Apparent watts}}{\text{True watts}} = \frac{\cos(\theta-\phi)\,.\,\cos\phi}{\cos\theta}$$

$$= \frac{1+\tan\theta\,.\,\tan\phi}{1+\tan^2\phi} \quad . \quad . \quad . \quad (1)$$

The circuit *cd* need only possess a self-induction *l*, even if an ammeter or dynamometer form part of it, but the circuit *ab* may have mutual induction and capacity as well as self-induction. If therefore we write expression (1) in the form

$$\frac{1+\frac{Lp}{R}\cdot\frac{lp}{r}}{1+\left(\frac{lp}{r}\right)^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

as we did in 1888, where p equals 2π times the frequency, it must be remembered that while l and r are the true values of the self-induction and resistance of *cd*, L and R are only the *effective* self-induction and resistance of *ab*. Hence, as Mr. Blathy suggested in the 'Electrician' for 1888, it is better to leave our expression for the ratio of the apparent to the true watts in the general form as given in (1) rather than to put it in the derived form as given in (2).

ϕ will generally be positive if the resistance of *cd* is small; but, if *cd* contains a doubly-wound high resistance-coil, as is generally the case when *cd* is the fine-wire circuit of a watt-meter, then it is quite possible to make ϕ positive, nought, or negative. θ may, of course, be also positive, nought, or negative, depending on whether the self and mutual induction effects preponderate or not over the capacity effect. It is therefore possible to have either θ or ϕ, or both, positive or negative.

The apparent watts will therefore be :—

too large if θ and ϕ be both of the same sign and $\theta > \phi$;

too small if { (1) θ and ϕ be both of the same sign and $\theta < \phi$;
(2) θ or ϕ be of different signs ;

correct if { (1) θ and ϕ be equal ;
(2) ϕ be nought.

Now ϕ can be made very small in one or other of three ways :—

1. Use some method of testing, like that shown in figures 1, 3, 4, 5, 6, and 8, which does not require any measuring instrument to be placed in the non-inductive circuit *cd*.

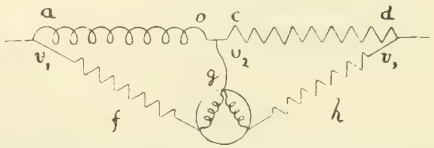
2. Use a wattmeter (fig. 9), and make the capacity of the stationary doubly-wound resistance-coil exactly balance the self-induction of the suspended and the stationary coils.
3. Make the resistance of the fine-wire circuit, *cd*, of the wattmeter small. For with a given P.D. between the terminals of *cd* the same deflexion of the measuring instrument can be obtained for different values of the resistance of *cd* if we make the number of turns in the coil or coils of the measuring instrument in *cd* proportional to the resistance *cd*. But the self-induction of the coil or coils is proportional to the square of the number of turns, and therefore proportional to the square of r for a given deflexion of the measuring instrument. Hence $\tan\phi$ can be made as small as we like for a given value of p by making the resistance of *cd* small.

This suggests a current method of measuring the power given to any circuit which is no more wasteful of power than the methods shown in figures 2, 3, 5, and 7; and which, although not so accurate as those shown in figures 3 and 5, is as accurate as those shown in figures 2 and 7. The method is simply to use a wattmeter (fig. 9), but having both its coils made of thick wire, or, as this may be called a split dynamometer, the method consists in using a split dynamometer having one of its coils in the circuit *ab* (the power given to which we desire to measure) and the other coil in a circuit *cd* parallel to *ab*. The power will be given at once by r times the reading of the instrument and with but a very small error if r be small.

V.

Mr. Rimington has suggested a method of measuring the mean value of the product $(v_1-v_2)(v_2-v_3)$ (fig. 9) by means of a dynamometer, each of whose coils is in circuit with a high resistance, joined up as shown in figure 10.

Fig. 10.



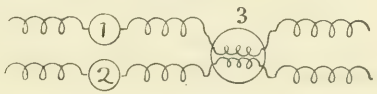
The objection to this method is as follows:—By making the time-constants of each of the circuits of the dynamometer *afg*,

d h g equal to one another, we can, no doubt, make the difference of phase in the two currents passing through the dynamometer exactly the same as the difference in phase between the current through *ab* and the P.D. at the terminals of *ab*; but we cannot make the currents through the dynamometer coils independent of the rate of alternation. Hence, if this instrument be employed for measuring the power given to *ab* in the way shown in figure 10, it must be calibrated for each rate of alternation of the current.

But although this defect exists in the employment of Mr. Rimington's high-resistance split dynamometer for the measurement of power, it can be used without error for measuring the phase-angle between *two P.D.s in series* by a method analogous to that employed by Mr. Blakesley for measuring the phase-difference between *two currents in parallel*.

Fig. 11 shows Mr. Blakesley's method: the dynamo-

Fig. 11.

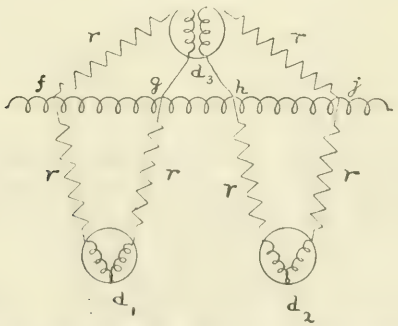


meters 1 and 2 give respectively the mean squares of the currents in the two circuits, and the dynamometer 3 the mean product of the two currents; and from the three readings we have, as is now well known,

$$\cos\theta = \sqrt{\frac{\text{Square of reading of 3}}{\text{Reading of 1} \times \text{Reading of 2}}},$$

where θ is the angle of lag.

Fig. 12.



Now let *f g* and *h j* be two circuits in series (fig. 12), and let it be required to find the angle of phase-difference θ

between the P.D. at the terminals of fg and the P.D. at the terminals of hj. Connect up the high-resistance dynamometer successively as shown, and let d_1, d_2, and d_3 be the three deflexions obtained.

Each circuit of the dynamometer consists of a coil of fine wire, and a non-inductive high resistance in series with it. Let r be the total resistance of each circuit, and let ϕ be the angle of lag between a current in either circuit of the dynamometer and the P.D. at its terminals.

Let V_1' and V_2' be the maximum values of the P.D. between f and g, and between h and j respectively, then

$$d_1 \propto \tfrac{1}{2}\left(\frac{V_1'}{2r}\right)^2 \cos^2\phi,$$

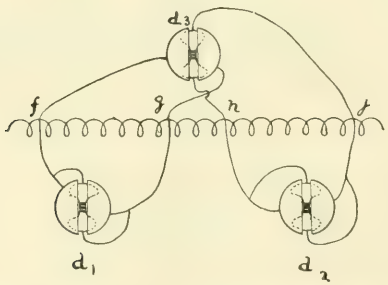
$$d_2 \propto \tfrac{1}{2}\left(\frac{V_2'}{2r}\right)^2 \cos^2\phi,$$

$$d_3 \propto \tfrac{1}{2}\left(\frac{V_1'}{r}\cos\phi \times \frac{V_2'}{r}\cos\phi\right)\cos\theta,$$

$$\therefore \quad \cos\theta = \sqrt{\frac{d_3^2}{16\,d_1 d_2}}.$$

Figure 13 shows the way in which the Blondlot and Curie double-needle electrometer can be successively connected up

Fig. 13.



so as to obtain, from the readings d_1, d_2, d_3, the angle of phase-difference between the P.D. at the terminals of fg, and the P.D. at the terminals of hj, the formula being, of course,

$$\cos\theta = \sqrt{\frac{d_3^2}{d_1 \times d_2}}.$$

I we desire to measure the angle of lag between the current in any circuit ab and the P.D. between its terminals, we

can employ either the three-voltmeter method (fig. 1) or either of its analogues, viz. the three-ammeter method (fig. 2), or the one-voltmeter and two-ammeter method (fig. 3). The formulæ giving the cosine of the lag angle for the three methods are, respectively,

$$\cos\theta = \frac{V_3^2 - V_1^2 - V_2^2}{2V_1V_2},$$

$$\cos\theta = \frac{A_3^2 - A_1^2 - A_2^2}{2A_1A_2},$$

$$\cos\theta = \frac{A_3^2 - A_1^2 - \left(\frac{V}{r}\right)^2}{2A_1\frac{V}{r}},$$

V_1, V_2, V_3, A_1, A_2, A_3, and V being the readings of the instruments in the different cases.

XXIX. *A Kinetic Theory of Solids, with an Experimental Introduction.* *By* William Sutherland.

[Continued from p. 43.]

Young's *Modulus.*

1. The experimental determinations that have hitherto been made of the temperature variations of Young's Modulus have been made for the most part by the static method, the difficulties of which detract from its trustworthiness; for example, Wertheim, by the static method, found the Young's Modulus of iron and silver to increase with rising temperature, though we now know that it diminishes. Kupffer (*Mém. de l'Acad. Impér. des Sc. de St. Pét.* 6 sér. t. 6) devised a convenient modification of the kinetic method (by lateral vibrations) which lent itself well to the measurement of the temperature effect, but used an erroneous formula for calculating the modulus from his measurements. Zöppritz (Pogg. *Ann.* cxxviii.) has recalculated with a correct theory the right values of the modulus of various metals at ordinary temperature from Kupffer's data. I recalculated the values at other temperatures, but found the temperature interval of about 30° C. too small to give trustworthy results. Accordingly I undertook a series of measurements by Kupffer's method.

The method consists in causing a rod of the metal to vibrate laterally with one end clamped and the other free, first with the free end vertically above the clamped one, and next under it.

The rod is either loaded or not loaded at the free end according to convenience. Kupffer's error came in in the method in which he tried to eliminate the influence of gravity. Of course, if the rods were made to vibrate in a horizontal instead of a vertical plane, gravity would have no appreciable effect if the rods were stiff enough and unloaded, but the bending effect of a load must needs interfere; and in the case of lead and tin wires, for example, even when unloaded, it is impossible to make them vibrate in a horizontal plane. A lead wire which will collapse at once if held horizontally at one end, will stand vertically if clamped at the bottom and execute vibrations without collapse; and even at temperatures at which, when the bottom is clamped, vibrations become impossible through instability, it is always possible, with the top clamped, to get stable vibrations.

Thus, to get values of Young's modulus by Kupffer's method at any temperature requires only a correct method of allowing for the action of gravity in affecting the period of vibration.

The advantages of Kupffer's method are several: it can be applied to convenient sizes of material, while the static method, to give accurate results, necessitates the use of long wires; by loading the end of the vibrating piece its period can be made such as is easily measured without special recording-appliances, and is obtainable by a mere counting of vibrations in a measured time. If desired, the method could easily be used for determining the influence of stress on the value of Young's modulus; by loading the free end, the value of the modulus could be found under stresses right up to the breaking load.

Zöppritz (Pogg. *Ann.* cxxviii.) has given the theory of the effect of gravity on unloaded bars, but the case of loaded bars has not, so far as I am aware, been solved in a form suitable for practical use; and as freedom to load at will the specimen under experiment is one of the best points about the method, it will be as well to give first the theory of the lateral vibration of a loaded bar under gravity.

A slight adaptation of a method of calculation given by Rayleigh in his 'Theory of Sound,' vol. i. chapter 8, gives a close enough solution for practical purposes. He shows that the period of a laterally-vibrating bar can be got approximately by supposing the bar bent statically by a deflecting force applied to the free end and then allowed to move, so that at any time t from the moment of release the deflexion of any point on the bar is to its original deflexion in the ratio $\cos 2\pi nt$ to unity. Then, by equating the maximum value of the potential energy during the motion to the maximum value

of the kinetic energy, a value of the frequency n is obtained, which is approximately identical with that given by the complete theory of the lateral vibrations of a bar. Accordingly it is only necessary to add to the potential energy of bending that due to gravity to get an approximate solution. Suppose clamped at either the top or bottom a uniform vertical bar of length l, density ρ, section σ, radius of gyration of section k, mass m, loaded with mass M, which has its centre of mass at distance l' from the clamped end, and suppose the free end deflected with force F. Now the tendency of the weight of M is to increase the bending effect of F when M is up, and to diminish it when M is down ; but for small displacements this difference in the effect of the weight of M in the two cases can be neglected. If y is the deflexion of the point at distance x from the clamped end, then the form of the rod is given by

$$y=\frac{\mathrm{F}}{6\mathrm{B}}(x^3-3lx^2),$$

where $\mathrm{B}=qk^2\sigma$, in which q is Young's modulus.

Then, according to the approximate method, the form at time t is

$$y=\frac{\mathrm{F}}{6\mathrm{B}}(x^3-3lx^2)\cos 2\pi nt.$$

The potential energy of bending is

$$\mathrm{V}=\tfrac{1}{2}\int \mathrm{B}\left(\frac{d^2y}{dx^2}\right)^2 dx.$$

To find the potential energy due to gravity we have to determine how much each point of the rod is vertically displaced on bending. Let ds be an element of length in the bent rod, then

$$ds=dx\sqrt{1+(dy/dx)^2}=dx\sqrt{1+\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2(x^2-2lx)^2}$$

$$=dx\left\{1+\tfrac{1}{2}\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2(x^2-2lx)^2\right\}\text{ approximately ;}$$

$$\therefore s=x+\tfrac{1}{2}\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2\left(\frac{x^5}{5}-lx^4+\frac{4l^2x^3}{3}\right),$$

so that $s-x$, the required vertical displacement of the element at length s along the rod,

$$=\tfrac{1}{2}\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2\left(\frac{x^5}{5}-lx^4+\frac{4l^2x^3}{3}\right).$$

Let λ be the mass of unit length, then the gravitational potential energy of the whole rod is

$$\int_0^l g\lambda(s-x)dx = g\lambda\tfrac{1}{2}\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2\left\{\frac{x^6}{30}-\frac{lx^5}{5}+\frac{l^2x^4}{3}\right\}_0^l$$
$$= g\lambda\tfrac{1}{2}\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2\frac{l^6}{6} = g\tfrac{1}{2}\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2\frac{ml}{6}.$$

The gravitational potential energy due to the vertical displacement of M is $\mathrm{M}g(l'-\mathrm{X})$, where X is the x coordinate of the point originally at distance l' from the clamped end.

$$l'-\mathrm{X} = \tfrac{1}{2}\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2\left(\frac{l'^5}{5}-l'^5+\frac{4l'^5}{3}\right)$$
$$= \tfrac{1}{2}\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2\frac{8}{15}l'^5.$$

Hence the gravitational potential energy of the mass M is

$$\tfrac{1}{2}\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2\frac{8}{15}\mathrm{M}gl'^5;$$

and the total potential energy of the loaded bent rod is

$$\tfrac{1}{6}\frac{\mathrm{F}^2}{\mathrm{B}}l^3 \pm \tfrac{1}{2}\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2 g\left(\frac{ml^5}{6}+\frac{8}{15}\mathrm{M}l'^5\right),$$

the two signs corresponding to the two cases of free end up or down.

For the kinetic energy we have $\mathrm{T}=\frac{1}{2}\int\rho\sigma(dy/dt)^2dx$; neglecting, as is usual, the effect of the slight rotatory motion of the bar,

$$\mathrm{T} = \left(\frac{\mathrm{F}}{6\mathrm{B}}\right)^2\left(2\mathrm{M}l'^6+\frac{33}{70}ml^6\right)4\pi^2n^2\sin^2 2\pi nt.$$

Hence for n, the number of vibrations per second, we get

$$4\pi^2n^2\left(\frac{\mathrm{F}}{6\mathrm{B}}\right)^2\left\{2\mathrm{M}\left(\frac{l'}{l}\right)^6+\frac{33}{70}m\right\}l^6 = \tfrac{1}{6}\frac{\mathrm{F}^2}{\mathrm{B}}l^3 \pm \tfrac{1}{2}\left(\frac{\mathrm{F}}{2\mathrm{B}}\right)^2 g\left(\frac{ml^5}{6}+\frac{8}{15}\mathrm{M}l'^5\right)$$

But this is only an approximation; in the rigorous theory when $\mathrm{M}=0$ the fraction 33/70 is replaced by $6/1{\cdot}8751^4$ (Rayleigh, vol. i. p. 234). Let us so replace it, and we have an equation that goes very near to the truth in all cases, namely

$$\text{(A)}\quad 4\pi^2n^2\left\{2\mathrm{M}\left(\frac{l'}{l}\right)^6+\frac{6m}{1{\cdot}8751^4}\right\}l^3 = 6\mathrm{B}\pm\frac{9g}{2}\left(\frac{ml^2}{6}+\frac{8\mathrm{M}l'^5}{15l^3}\right).$$

When $\mathrm{M}=0$ we have the case of the bar unloaded but affected by its own weight, then

$$4\pi^2n^2\frac{6ml^3}{1{\cdot}8751^4} = 6\mathrm{B}\pm\frac{9g}{2}\frac{ml^2}{6}.$$

This is the case treated by Zöppritz, whose solution in our symbols is

$$4\pi^2 n^2 \frac{6ml^3}{1{\cdot}8751^4} = 6\mathrm{B} \pm \frac{9{\cdot}17g}{2}\frac{ml^2}{6},$$

which differs only slightly from ours in the numerical coefficient of the small term.

Let n_1 n_2 be the numbers of vibrations per second when the bar vibrates with the loaded end up and down respectively, then

$$\text{(B)} \quad \left\{2\mathrm{M}\left(\frac{l'}{l}\right)^6 + \frac{6m}{1{\cdot}8751^4}\right\} l^3 4\pi^2(n_1^2+n_2^2) = 12\mathrm{B};$$

and the effect of gravity is eliminated. This, then, is the equation to use with Kupffer's method.

When $\mathrm{M}=0$,

$$\mathrm{B} = 2\pi^2(n_1^2+n_2^2)\frac{l^3 m}{1{\cdot}8751^4},$$

but $\mathrm{B}=qk^2\sigma$,

$$\therefore \quad q = 2\pi^2(n_1^2+n_2^2)\frac{l^3 m}{1{\cdot}8751^4}\frac{1}{k^2\sigma}.$$

If the bar is of circular section, $k^2=r^2/4$ and $\sigma=\pi r^2$; and then

$$q = 8\pi(n_1^2+n_2^2)\frac{l^3 m}{r^4 1{\cdot}8751^4} = 8\pi^3(n_1^2+n_2^2)\frac{l^5 m}{\pi^2 r^4 l^2\, 1{\cdot}8751^4};$$

$$\text{(C)} \quad q = 8\pi^3(n_1^2+n_2^2)\frac{l^5\rho^2}{m\, 1{\cdot}8751^4}.$$

Equation (B) can be confirmed by Kupffer's experiments. For one and the same bar the left-hand side is to be constant for all values of the load. For a steel bar 49·66 inches long and weighing 1·5848 Russian pounds, we have the following values of the left-hand side for the following values of M :—

M in Russian pounds...	0	0·6852	1·0644	1·8173
	5·669	5·650	5·630	5·600

Again, for a piece of the same bar 40·08 inches long and weighing 1·2792 Russian pounds, we have the values:—

M...	0	0·6852	1·0644	1·8173	3·2970	4·0566
	10·63	10·60	10·58	10·52	10·45	10·39

In both cases the number which ought to be constant shows a slight diminution with increasing load, which is easily accounted for, and the approximation to constancy is close enough to warrant the use of the formula for the determination of Young's modulus. To satisfy myself of the complete

applicability of the formula, I made copper and magnesium wires vibrate unloaded both in the two vertical positions and in the horizontal; calling n_3 the number of vibrations per second in the horizontal position, I found that $n_1^2+n_2^2=2n_3^2$, as should be, to a high degree of accuracy. But there is another check which can always be applied to any set of experiments. The equation (A) shows that

$$(\mathrm{D})\quad (n_1^2-n_2^2)4\pi^2\left(2\mathrm{M}\left(\frac{l'}{l}\right)^6+\frac{6m}{1{\cdot}8751^4}\right)l^3=9g\left(\frac{ml^2}{6}+\frac{8\mathrm{M}l'^5}{15l^5}\right),$$

so that $n_1^2-n_2^2$ is quite independent of the elastic properties of the bar, and has a calculable value. It is therefore a check on the method to see that the observed value of $n_1^2-n_2^2$ is equal to the calculated. In the experimental values about to be given this method of verification will be applied, and it will be seen that in any case where it is possible to make observations with only one vertical position of the bar, the equation (A) can be safely used for the calculation of Young's modulus.

Of course, where the Young's modulus of a substance varied appreciably with stress, it would not be possible to eliminate the action of gravity, as in equations (B) and (C), but equation (A) could be used.

Experiments.—The vibrations were carried out in the same box heated in the same manner as in the Rigidity experiments. The rod or wire that was to vibrate could be clamped at the middle point of either the top or the bottom of the box, and executed its vibrations freely inside. To secure accuracy in determining the period of the swing the vibrations had to be reinforced, and this was done by means of a thread passing horizontally from the free end of the wire to the outside; by means of the thread a slight periodic impulse could be imparted to the vibrating wire at the middle of a swing; a little practice enabled one to attain a high degree of accuracy with even lead and tin wires in determining the number of vibrations per second. Every value given in what follows was derived from several hundreds of swings.

In all cases except that of tin wire, the wires vibrated unloaded, and accordingly equation (C) applies.

Lead.—Commercial wire, the same as that used in the Rigidity experiments. l 38·1 cm., m 14·05 grm., ρ 11·4.

n_1 denotes the number of vibrations per second when the free end is down, and n_2 when up; q denotes Young's modulus, and will be given in terms of grammes weight per sq. cm.

Temp. C.	18°	65°	103°
n_1	2·87	2·74	2·65
n_2	2·50	2·35	2·17
$10^{-6}q$	220	198	178
$n_1^2-n_2^2$	1·99	1·99	2·31

The theoretical value of $n_1^2-n_2^2$ according to equation (D) is 2·02, so that the formula is well verified in this case.

Magnesium.—Fine commercial wire, as used in rigidity experiments. l 43·9 cm., m ·201 grm., ρ 1·74.

Temp. C.	17°	68°	104°
n_1	2·09	2·05	1·97
n_2	1·62	1·57	1·54
$10^{-6}q$	352	335	314
$n_1^2-n_2^2$	1·75	1·74	1·51

The theoretical value of $n_1^2-n_2^2$ is 1·75. It is to be remembered that in the case of the metals, $n_1^2-n_2^2$, which measures the effect of gravity as compared with that of elasticity, is very small, and that on account of experimental errors only general agreement in magnitude is to be expected between the experimental and theoretical values of $n_1^2-n_2^2$. For example, the discrepant experimental number 1·51 just given illustrates the amount of departure that may occur.

Zinc.—The thin rod prepared for the Rigidity experiments. l 63·5 cm., m 31·3 grm., ρ 7·04.

Temp. C.	16°	60°	103°
n_1	3·53	3·40	3·21
n_2	3·24	3·11	2·97
$10^{-6}q$	821	758	682
$n_1^2-n_2^2$	1·96	1·89	1·48

The theoretical value for $n_1^2-n_2^2$ is 1·21.

Copper.—Swedish wire for alloying gold. l 63·5, m 22·4, ρ 8·95.

Temp. C.	16°	102°	
n_1	3·11	2·98	
n_2	2·92	2·79	
$10^{-6}q$	1378	1260	
$n_1^2-n_2^2$	1·14	1·10	Theory 1·21.

Aluminium.—Fine commercial wire. l 56·5, m ·453, ρ 2·56.

Temp. C.	18°	102°	
n_1	1·605	1·559	
n_2	1·142	1·090	
$10^{-6}q$	662	616	
$n_1^2-n_2^2$	1·28	1·24	Theory 1·36.

Aluminium (unannealed).—Fine commercial wire. l 62·5, m ·5, ρ 2·56.

Temp. C.	18°	63°	104°	
n_1	1·335	1·319	1·295	
n_2	0·762	0·740	0·722	
$10^{-6}q$	602	584	561	
$n_1^2-n_2^2$	1·20	1·19	1·16	Theory 1·23.

Iron (specimen I.).—Commercial tough wire. l 66·7, m 4·04, ρ 7·55.

Temp. C.	18°	67°	103°	
n_1	1·830	1·811	1·804	
n_2	1·412	1·395	1·383	
$10^{-6}q$	2029	1984	1960	
$n_1^2-n_2^2$	1·35	1·33	1·34	Theory 1·15.

Iron (specimen II.).—Commercial wire (soft). l 67·2, m 9·88, ρ 7·55.

Temp. C.	18°	66°	102°	
n_1	2·662	2·636	2·608	
n_2	2·400	2·370	2·350	
$10^{-6}q$	2071	2024	1983	
$n_1^2-n_2^2$	1·33	1·33	1·28	Theory 1·14.

Tin.—A cast rod was hammered out to three times its length. To make the period conveniently measurable with a watch it was necessary to load this rod at the end. The length of the rod was 40·1 centim., and the distance of the centre of mass of the load from the clamped end l' 41·2, the mass of the rod m 16·2, and the mass of the load M 15·95, ρ 7·29.

Temp. C.	16°	66°	104°	
n_1	2·72	2·49	2·33	
n_2	2·34	2·12	2·00	
$10^{-6}q$	513	425	374	
$n_1^2-n_2^2$	1·92	1·71	1·43	Theory 1·73.

In the case of tin and lead I made experiments on a larger scale on the same pieces of pipe as were used in the Rigidity experiments. For a pipe of external radius r_2 and internal r_1 Young's modulus is given by the formula

$$q=\frac{8\pi^2 l^4 \rho (n_1^2+n_2^2)}{1{\cdot}8751^4 (r_2^2+r_1^2)}.$$

With the tin pipe of length 119·6 centim. and at a temperature of 18°, $n_1=3{\cdot}82$, $n_2=3{\cdot}73$, whence $10^{-6}q=421$ and $n_1^2-n_2^2={\cdot}68$, while according to theory $n_1^2-n_2^2={\cdot}64$.

With the lead pipe of length 121·9 and at temperature 23° $n_1=2{\cdot}53$, $n_2=2{\cdot}40$, whence $10^{-6}q=161{\cdot}7$ and $n_1^2-n_2^2={\cdot}641$, while the theoretical value of $n_1^2-n_2^2$ is ·635.

2. *Compilation of Data.*—As regards the variation of Young's modulus with temperature, Kupffer's vibrational method is so superior in accuracy to the static method, that even rough experiments like my own by Kupffer's method give far more trustworthy results than even the most careful and refined measurements yet made by the static method. Kupffer's own temperature-range was too small to give weight to his measurement; and as I know of no other measurements by his method, I must regard the data just given as the most trustworthy yet published. It is therefore hardly worth while quoting other results except those of Kiewiet, who (Wied. *Ann.* xxix.) applied a much more sensitive static method than the usual one, namely, the method of bending to zinc, tin, and copper. Kiewiet's values, in the case of tin, for the ratio of q at 60° and 104° to q at 16° are ·82 and ·67, while mine are ·83 and ·73; in the case of zinc at 60° and 103° and 16° the ratios found by Kiewiet are ·92 and ·87, while my values are ·92 and ·83. At 102° and 16° Kiewiet finds for rolled copper the ratio ·967, and for electrolytic copper ·934, while my number is ·914.

Except for copper the agreement of the two methods is good, all things considered.

In the following compilation as to the absolute values of Young's modulus at ordinary temperatures, these are the sources:—Wertheim, *Ann. de Ch. et de Ph.* 3 sér. t. xii.; Zöppritz's recalculation of Kupffer's data, Pogg. *Ann.* cxxviii.; Kupffer, *Cosmos*, 1860; Pisati, Wied. *Beibl.* i.; Tomlinson, Phil. Trans. 1883, and Proc. Roy. Soc. xlii. & xliii.; Macfarlane, *Encyc. Brit.*, article Elasticity; Miller, Wied. *Beibl.* xi.; Katzenelsohn, Wied. *Beibl.* xii.; Kiewiet, Wied. *Ann.* xxix.; Mercadier, *Compt. Rend.* cviii.; Amagat, *Compt. Rend.* cviii.; Cantone, Wied. *Beibl.* xiv.

When a specimen is known to have been unannealed it is marked (*u*).

Table VI.

Values of 10^{-6} times Young's Modulus at Ordinary Temperatures.

Metal.	$10^{-6}q$.	Authority.	Metal.	$10^{-6}q$.	Authority.
Copper	1254	Wertheim.	Aluminium ...	717	Kupffer.
	1183	Wertheim.		673	Tomlinson.
	1052	Wertheim.		705	Mercadier.
	1160	Tomlinson.		754	Katzenelsohn.
	1218	Tomlinson.		662	Sutherland.
	1143	Tomlinson.	(*u*)	602	Sutherland.
	1283	Kupffer & Zöppritz.	Tin.....	442	Wertheim.
				370	Wertheim.
	1231	Mercadier.		507	Kupffer.
	1231	Amagat.		277	Tomlinson.
(rolled)	1224	Kiewiet.		450	Kiewiet.
(electro).....	1225	Kiewiet.	(hammered)..	513	Sutherland.
	1300	Miller.	(pipe).....	421	Sutherland.
	1150	Macfarlane.	Lead	215	Wertheim.
	1200	Macfarlane.		185	Wertheim.
(*u*)	1323	Tomlinson.		173	Wertheim.
	1316	Tomlinson.		167	Tomlinson.
Silver	724	Wertheim.		255	Miller.
	753	Wertheim.		149	Amagat.
	714	Wertheim.		220	Sutherland.
	777	Kupffer & Zöppritz.	(pipe).....	161·7	Sutherland.
			Iron	1992	Wertheim.
	742	Tomlinson.		1941	Wertheim.
	799	Mercadier.		2079	Wertheim.
	736	Miller.		1861	Wertheim.
(alloy)	701	Katzenelsohn.		2006	Kupffer.
(*u*)	836	Tomlinson.		2103	Kupffer.
(*u*)	829	Tomlinson.		1981	Tomlinson.
Gold	637	Wertheim.		1881	Miller.
	599	Wertheim.		1902	Katzenelsohn.
	558	Wertheim.		2144	Pisati.
	741	Kupffer & Zöppritz.		2029	Sutherland.
				2071	Sutherland.
	834	Mercadier.	Nickel	2175	Tomlinson.
(alloy)	980	Katzenelsohn.		2310	Cantone.
(*u*)	860	Wertheim.		2248	Cantone.
(*u*)	864	Wertheim.	Cobalt	1817	Tomlinson.
(*u*)	813	Wertheim.	Palladium.....	1128	Wertheim.
Magnesium ...	431	Tomlinson.		979	Wertheim.
	352	Sutherland.	Platinum	1556	Wertheim.
Zinc	929	Wertheim.		1568	Wertheim.
	964	Wertheim.		1552	Wertheim.
	967	Kupffer & Zöppritz.		1437	Wertheim.
				1770	Kupffer.
	1031	Kiewiet.		1490	Tomlinson.
	1055	Miller.		1719	Katzenelsohn.
	821	Sutherland.		1967	Miller.
(*u*)	767	Tomlinson.		1491	Mercadier.
Cadmium	424	Wertheim.	(*u*)	1623	Tomlinson.
	531	Wertheim.	(*u*)	1622	Tomlinson.

These give us the following mean values of Young's modulus at 15° C. :—

TABLE VII.

10^{-6} times Young's Modulus at 15° C.

Cu.	Ag.	Au.	Mg.	Zn.	Cd.	Al.
1220	740	760	390	930	480	680
Sn.	Pb.	Fe.	Ni.	Co.	Pd.	Pt.
420	190	2000	2240	1820	1050	1600

In most cases these values must be close to the truth.

3. *Law of Variation of* Young's *Modulus with Temperature.* —By the light of the result for rigidity this law is easily found ; temperature must only occur in the ratio θ/T, where T is the melting-point ; and as a general survey of the values of Young's modulus for different metals at different temperatures shows that the modulus within our experimental range is a linear function of the temperature, it was easy to test whether the empirical equation $q/Q = 1 - a\theta/T$ would apply to all the metals, Q being the rigidity at absolute zero, and a a constant the same for all metals. The result was to find that $q/Q = 1 - \cdot 823t/T$ represents with considerable accuracy all the foregoing experimental results. But it is important to notice that this can only rank as an approximate empirical relation covering the range of temperature of my experiments, and cannot rank as a natural law in the same way as the rigidity relation $n/N = 1 - (\theta/T)^2$, because it does not cover the range of temperature right down to the melting-point ; the relation gives a finite value for Young's modulus at the melting-point, whereas it ought to give a zero value. The relation then does not give the general law sought, and is only mentioned here on account of its simplicity and the facilities it gives for getting approximate values of Q, the Young's modulus at absolute zero.

As a theoretical relation between Young's modulus and temperature will be investigated in the theoretical part of this paper, and the values of Young's modulus at absolute zero will be given there, there is no need to consider any further the empirical relation.

[To be continued.]

XXX. *Notices respecting New Books.*

The Structure of a Portion of the Sierra Nevada of California. By George F. Becker. Bullet. Geol. Soc. of America, vol. ii. 1891.

From the South Fork of the Stanilaus River to the Trucknee, a distance of about eighty miles, and for some thirty miles to the west of the eastern scarp of the range, Dr. Becker found the rocks to be chiefly granite and diorite overlain in part by andesite and basalt; and the area to have been glaciated up to the summits of the passes. The rocks are intersected by extremely numerous fissures,—vertical, diagonal, and horizontal; the last giving a terraced aspect to the granite, and the two former rendering it columnar. The fissures are more or less susceptible of being grouped as systems; and are found to be true fault-planes, with dislocations, slickensides, and slaty shearing. These multitudinous faultings are referred to a late Tertiary period, in part contemporary with the andesitic eruptions.

An inductive examination of dislocating forces treats of the physical characters of these faults and fissures in detail, both as to horizontal and vertical movements. The author shows "that the existence of the vertical fissure systems attended by evidences of compression leads inevitably to the theory of a horizontal thrust, which is further confirmed by the occurrence of relatively rare fissures dipping at angles of 45°." So also as to "the fissure systems formed by the vertical thrust, . . . the horizontal partings could be produced without raising the sheets of granite, while the vertical fissuring and faulting by the vertical thrust component involved either the raising of a sheet against gravity, or a downward movement into the underlying mass. When the vertical fissures and the horizontal fissures were once formed, the stress still present would be relieved rather by relative motion on these fissures than by the establishment of new ones."

The hypothesis of the tilting of the range, to account for the deep erosion of the river-beds, is not supported by Dr. Becker's observations. He considers that the fissure-systems broke up the area in such a manner that glaciers, which are really unequal to the excavation of valleys themselves, cleared away the movable débris from the surface, giving the country its peculiar physical features of cañons, out of shattered zones, and domes from isolated prismatic masses of rock.

Antiquities from under Tuolumne Table Mountain in California. By George F. Becker. Bullet. Geol. Soc. of America, vol. ii. 1891.

The occurrence of human bones and of grinding implements in the auriferous gravel under the lava at the foot of Table Mountain in California has been doubted, but Dr. Becker supports Prof. Whitney's announcement of these discoveries by further and independent evidence of the facts. Plant-remains, like those of Tertiary age,

with bones of extinct Mammalia, for instance *Rhinoceros hesperius* and *Mastodon americanus*, have been met with in this gravel. Flows of lava covered it; and the glaciation of the Sierra followed, leaving in ridges the lava-flows that had covered these old valley-gravels, and making new valleys out of the intermediate rock-margins of those gorges. Plate 7 represents the pestle and one of the two mortars found, with stone spear-heads, by Mr. Neale in 1870; and a woodcut shows a broken pestle found by Mr. Clarence King in 1869.

Dr. Becker gives some remarks on the correlation of the lavas and gravels with the eastern deposits; and proceeds to explain that the great valley of California was formerly a Pleistocene gulf, and the Pliocene animals may reasonably be supposed to have survived in the locality to a late period; also that a local glaciation, due to peculiar climatal conditions, may have occurred here after the more general Glacial Epoch.

At the reading of Dr. Becker's paper the Rev. G. F. Wright gave some further information on the subject, to the effect that another mortar had been found in the same gravel in 1887.

Notes on the Early Cretaceous of California and Oregon. *By* George F. Becker. Bullet. Geol. Soc. of America, vol. ii. 1891.

The definition of this group and its fauna is detailed, showing that the one group of strata in the Coast Ranges of California, called the Knoxville group, and the other near Horsetown in Shasta County, are probably equivalent to the Gault. In the Sierra Nevada these strata are intersected by numerous auriferous quartz veins; in the Coast Ranges they are extensively metamorphosed and yield quicksilver.

The same group is represented at Riddles, Douglas County, Oregon, and in Queen-Charlotte Islands. One of the leading fossils is the *Aucella*, characterizing strata of approximately the same age also in Alaska and British Columbia, and, according to Dr. G. M. Dawson, even as far north as Porcupine River within the Arctic Circle. Mr. J. S. Diller added the information that both the Knoxville and the Horsetown beds are well exposed in Tehama County, between the localities of California and Oregon referred to by Dr. Becker.

The Horsetown beds lie unconformably on nearly vertical slates, and the disturbance thus indicated was probably Post-Triassic; for in the Mineral-King district, about two miles from the summit of the western branch of the Sierra, vertical slates associated with eruptive granite contain casts of shells indicative of a Triassic fauna. The author adds—"The main mass of the granite of the Sierra is earlier than the *Aucella*-beds, and in part, at least, later than these Triassic beds. It is very probable that a granitic extrusion accompanied the disturbance which led to the nonconformity at Horsetown. In British Columbia Dr. Dawson has traced a Post-Triassic upheaval, which was accompanied by granites. This

seems to add one more to the many indications that the Pacific coast throughout North America, if not throughout the two Americas, has had a very similar history."

The Photochronograph and its Application to Star-Transits. By J. G. Hagen, S.J. (Stormont & Jackson, Printers, Washington, D.C.: 1891.)

This is a pamphlet of 36 pages and 2 plates describing experiments and results in photographing star-transits at the Georgetown College Observatory. The work had its origin in a visit made by Prof. F. Bigelow and Mr. G. Saegmüller to the Observatory named in the summer of 1889, and it is confidently stated that "this method of letting the sensitive plate take the place of the eye and the chronograph seems to have a great future." It is claimed that the entire absence of personal equation in the results, and the fact that the probable errors are smaller than in the usual plan, give to the photographic method a practical importance and superiority which cannot fail to be recognized. "A photographic transit is, on the whole, more laborious than one taken by the chronograph, yet it certainly makes it possible for us to eliminate the personal equation in all cases where such elimination must be purchased at any cost. As an example we need only mention *longitude* determinations. The usual exchange of the observers, so expensive in time and money, is, by the photographic method, rendered unnecessary and even useless. If the photochronographs at the two stations are worked by the same clock at either station, or at an intermediate one, the sensitive plates will record the difference of the two meridians without the interference of the observers." The experiments are to be continued, the peculiar errors of the method are to be studied, and it is proposed to test its efficiency in regular zone work.

XXXI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 141.]

June 24, 1891.—Sir Archibald Geikie, D.Sc., LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. "On Wells in West-Suffolk Boulder-clay." By the Rev. Edwin Hill, M.A., F.G.S.

It might be supposed that in a Boulder-clay district water could only be obtained from above or from below the clay. But in the writer's neighbourhood the depths of the wells are extremely different, even within very short distances; and since the clay itself is impervious to water, he concludes that it must include within its mass pervious beds or seams of some different material which communicate with the surface. It would follow that this Boulder-clay is not a uniform or a homogeneous mass.

The visible sections are only those given, at hand by ditches, and at a considerable distance north and south by pits at Bury St. Edmunds and Sudbury. The appearances in these harmonize with that conclusion. Conclusion and appearances differ from what we should expect on the theory that this Boulder-clay was the product of the attrition between an ice-sheet and its bed.

2. "On the Melaphyres of Caradoc, with Notes on the Associated Felsites." By Frank Rutley, Esq., F.G.S.

Within very limited areas the melaphyres of Caradoc differ considerably in texture and in structure, some having once been basalt-glass or andesite-glass (such being the superficial portions of a lava-stream); others have possessed a certain amount of interstitial glass, which has subsequently been rendered more or less opaque by the development of magnetite, while at times it appears to have been converted into a palagonitic substance. In some of the rocks the crystalline texture is very fine, in others comparatively coarse. Near the summit of Caradoc is a basalt-tuff or andesite-tuff.

The melaphyre or dolerite of Little Caradoc differs from the lavas in that the augite remains fresh and the felspars are altered, while in the lavas of Caradoc proper the pyroxenic constituent is decomposed and the felspars remain as a rule unaltered.

Whether the melaphyre of Little Caradoc may be regarded as a neck from which the lavas lying to the south-west of it emanated, is a point which can only be demonstrated by further field-work.

The author considers that further investigation may prove beyond dispute that the associated felsites are rhyolites of which the original structures have as a rule been almost entirely obliterated. In an appendix further evidence is adduced in favour of the original rhyolitic nature of these felsites, and a fragmental rock from Bowdler's Chair is described as unquestionably a rhyolite-tuff.

3. "Notes on the Geology of the Tonga Islands." By J. J. Lister, Esq., M.A.

The islands of the Tonga group are situated on a long ridge which rises from deep water on either side to within a thousand fathoms of the surface of the sea. The general direction of the ridge is N.N.E. and S.S.W.

(1) A line of volcanoes, some active, some extinct, traverses the group. Continued southward, the direction of the line passes through the volcanoes of the Kermadec group, and those of the Taupo zone of New Zealand; while to the north it cuts the line of the Samoan volcanoes at right angles.

(2) Besides the purely volcanic islands there are some formed by submarine eruptions, whose layers have been laid out under water and since elevated, with or without a covering of limestone.

(3) The remaining islands are formed entirely of limestone.

Eua is an example of the second group. The volcanic basis consists for the most part of beds laid out beneath the sea, and some of

the upper ones contain pelagic shells. Dykes of augite and hypersthene-andesite project on the shore, and a representative of the plutonic series occurs. There is evidence that the island has been elevated and again submerged prior to the elevation which has raised it to the present height. The volcanic basis is largely invested with limestone, and this rock forms the summit 1078 feet above sea-level. Sections show that it is a shallow-water deposit.

Of the purely limestone structures, Tongatabu, Nomuka, and the long reef on which the larger islands of the Hapaii group are situated form more or less complete atolls, all of which have been elevated to a greater or less extent.

The Vavau group is remarkable for its very indented contour, suggesting the idea that it rests on a much denuded basis. Both here and at Eua there are raised limestone formations with atoll or barrier-like contours; and there is some direct evidence to show that these have been formed without the aid of subsidence.

The presence of islands formed of volcanic materials laid out in layers beneath the sea, and the manner in which the recently formed Falcon Island is now being reduced to the condition of a submarine bank, suggest that the atolls of the group may rest on similarly formed foundations.

4. "On the Inverness Earthquakes of November 15th to December 14th, 1890." By C. Davison, Esq., M.A.

In this paper the author gives reasons for supposing that the Inverness earthquakes of last year were due to the subsidence of a great wedge of rock included between a main fault and a branch one; and he considers that there is little doubt that these recent earthquakes were the transitory records of changes that, by almost indefinite repetition in long past times, have resulted in the great Highland faults.

XXXII. *Intelligence and Miscellaneous Articles.*

ON THE DETERMINATION OF THE DIELECTRIC CONSTANT OF GLASS BY AID OF VERY RAPID ELECTRICAL OSCILLATIONS. BY R. BLONDLOT.

VERY rapid electrical oscillations, such as are produced by Hertz's apparatus, have been utilized by Prof. J. J. Thomson for the measurement of the dielectric constant*. Prof. Thomson draws from his experiments the following conclusion: "for vibrations whose frequency is .... 25,000,000 per second, the specific inductive capacity [of glass] is very nearly equal to the square of the refractive index, and is very much less than the value for slow rates of reversals."

As regards this conclusion we might demur to the use of the

* J. J. Thomson, "Specific Inductive Capacity of Dielectrics when acted on by very rapidly alternating Electric Forces," Proc. Roy. Soc. June 20, 1889.

formula which gives the period of the oscillations, a formula the tenability of which is doubtful in the case of very rapid oscillations. More recently, E. Lecher has measured the dielectric constants of several substances by the aid of a method founded also on the determination of the wave-length of very rapid oscillations, but without employing any formula.

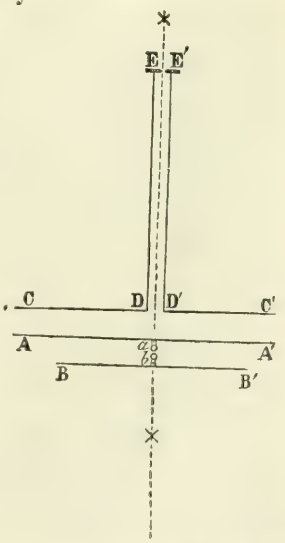
The conclusions of M. Lecher are diametrically opposed to those of Prof. Thomson: "Not only," says he, "does the dielectric constant, calculated by the aid of the capacity, not become smaller for very rapid oscillations, but it even considerably increases."

These contradictory conclusions have led me to engage in new researches; the method which I have adopted is based on the employment of very rapid oscillations, but I do not make use of any formula.

A large rectangular plate of copper A A′ is fixed vertically; a second, smaller plate B B′ forms a condenser with the first. This condenser can discharge itself by the intermediation of the knobs *a* and *b*; *a* is in communication with the gas-pipes, *b* with one of the poles of an induction-coil the other pole of which communicates with the gas-pipes. When the coil is working the condenser A B is the seat of oscillatory charges and discharges the period of which is of the order of the $\frac{1}{25,000,000}$ of a second.

We have thus in the space situated on the side of A A′ opposed to B B′ a periodic electromagnetic field which—and this is the chief point—has × × as the plane of symmetry.

Let us fix in this field two square plates C D, C′ D′ parallel to A A′ and symmetrical with respect to × ×, and then solder to the middle points D, D′ of their inner edges two wires terminating at E and E′ in two carbon points kept facing each other at a very small distance apart.



Although the coil is working, we do not observe any light between E and E′; this results from the symmetry of the apparatus. If we interpose a glass plate between A A′ and C D, sparks immediately pass between E and E′; this is caused by the induction received by C D becoming less strong than that received by C′ D′.

Let us now interpose between A A′ and C′ D′ a plate of sulphur; if we give to it such a thickness that the inductive action on C′ D′ is equal to that on C D, the sparks disappear between E and E.′ Conversely, the disappearance of sparks between E, E′ indicates

that the inductions transmitted to C D and C′ D′ are equal; it is sufficient therefore to measure the thicknesses of the dielectric plates to determine by an easy calculation the ratio of the dielectric constants of glass and sulphur. By means of experimental precautions which I cannot mention here I have been able to render this method sensitive and exact.

The glass plate which I employed was exactly 3 centim. thick. For the other side, I cast two plates of sulphur in the form of prisms of the same angle, in such a manner that by clipping them together, as in Babinet's compensator, a plate with parallel faces was formed the thickness of which could be varied. I found 3·15 centim. for the thickness of the plate of sulphur which exactly compensated the plate of glass. To complete the determination of the dielectric constant of glass that of sulphur had to be obtained; this was easy, since sulphur is a nearly perfect dielectric. I employed the method indicated by M. J. Curie* and found the number $2{\cdot}94=(1{\cdot}67)^2$.

This result is almost identical with that of Prof. J. J. Thomson. Maxwell's law is not exactly verified, as the mean index of my plate of glass is about 1·51, but the difference is much less than that given by the values of dielectric constants obtained by the aid of slower methods. My conclusion is the same as that of Prof. J. J. Thomson.—*Comptes Rendus*, May 11, 1891, p. 1058.

ON AN IMPROVED METHOD OF DETERMINING SPECIFIC HEAT BY MEANS OF THE ELECTRICAL CURRENT. BY PROF. PFAUNDLER,

The method published in 1869, which depends on Joule's law according to which the same current develops in spirals of wire arranged in series quantities of heat which are proportional to the resistances, has hitherto met with but few applications, owing to the fact that it is only applicable to nonconducting liquids. The author has got rid of this objection by replacing the spirals of wire by thin glass spirals filled with mercury. He obtained also greater accuracy and certainty by interposing these resistances as branches in a Wheatstone's bridge, so that it was possible to control the ratio of the resistances during the passage of the current and keep it constant. Slight alterations of the resistances were compensated by placing glass threads in the straight ends of the tubes which contained the mercury. In other cases those alterations were measured by displacing the contact-key, and in this way the result was corrected.

The comparative measurement of the rise of temperature is made more sensitive by the aid of a thermopile.

Experiments are communicated which show the applicability of the method both for direct and alternating currents.—*Wiener Berichte*, April 9, 1891.

* *Ann. de Chim. et de Phys.* 1889.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

SEPTEMBER 1891.

XXXIII. *Some Applications of Physics and Mathematics to Geology.* By C. CHREE, *M.A., Fellow of King's College, Cambridge**.

PART I. *Some Physical and Mathematical Data.*

MANY of the terms employed in treating of the properties and conditions of matter have in common use a somewhat vague meaning. The meaning, so far as clearly outlined, is also only too often different from that which the physicist intends to convey. As regards terms such as *rigid*, *solid*, *plastic*, *viscous*, &c. it seems to me that even eminent geologists are apt to be misled by the popular usage, so that they fall into error respecting the data which mathematical and physical science places at their disposal. It thus seems advisable on the present occasion to clear the ground by briefly considering the sense attached to these terms by the more exact school of physicists. To render the following statements intelligible it is necessary to explain the meaning scientifically attached to the terms *stress* and *strain*. By stress is meant a force referred to unit of area of the surface across which it acts, by strain the increase in the distance between two material points divided by the original distance. For instance if a vertical bar n square inches in cross section fixed at the upper end, sustain a load of t tons, and the load be uniformly distributed over the cross section, the longitudinal stress is tn, taking the square inch as unit of area

* Communicated by the Author.

and the weight of one ton as unit of force. If a portion of the bar increase in length from 100 to 100·01 inches, and the increase be uniformly distributed over the portion lengthened, the longitudinal strain is $(100{\cdot}01-100)\times 10^{-2}$, or ·0001.

The writers who have had most influence on the present scientific usage of English terms dealing with physical properties are unquestionably Professor Clerk Maxwell and Sir William Thomson. The former gives the following definitions in his 'Theory of Heat'* :—"A body which when subjected to a stress experiences no strain would, if it existed, be called a Perfectly Rigid Body. There are no such bodies. . . ."

"A body which when subjected to a given stress at a given temperature experiences a strain of definite amount, which does not increase when the stress is prolonged, and which disappears completely when the stress is removed, is called a Perfectly Elastic Body."

"If the form of the body is found to be permanently altered when the stress exceeds a certain value, the body is said to be soft or plastic, and the state of the body when alteration is just going to take place is called the Limit of Perfect Elasticity."

"If the stress, when it is maintained constant, causes a strain . . . which increases continually with the time, the substance is said to be viscous."

A viscous material may be either solid or fluid. It is regarded by Maxwell as fluid when any stress, *however small*, produces a constantly increasing strain. Maxwell draws a distinction between elasticity of bulk and elasticity of shape—the latter being peculiar to solids—which is more fully treated of by Sir W. Thomson. A body possesses perfect elasticity of bulk when on the removal of the stress it returns to its original volume, even though the form of its surface be permanently altered. Both writers regard it as certain that solid bodies will retain perfect elasticity of bulk under compressive stresses which far exceed the limit of elasticity of shape. The following statement embodies the views of Sir W. Thomson†:—"If we reckon by the amount of pressure, there is probably no limit to the elasticity of bulk in the direction of the increase of pressure for any solid or fluid; but whether continued augmentation produces continued diminution of bulk towards zero without limit, or whether for any or every solid or fluid there is a limit towards which it

* 5th edition, chapter xxi.

† Mathematical and Physical Papers, vol. iii. pp. 7–8.

may be reduced in bulk, but smaller than which no degree of pressure, however great, can condense it, is a question which cannot be answered in the present state of science."

Maxwell, by denying the existence of a perfectly rigid body, maintains that every solid can sustain stress or transmit force only by suffering strain. Thus on depositing a feather on the most solid block of iron we produce in the iron a system of strains, infinitesimally small it is true, but whose existence can no more be questioned than the existence across the surface separating the iron and the feather of forces balancing the portion of the feather's weight left uncompensated by the air-pressure. The hypothesis quoted above from Sir W. Thomson, that there may be a limit beyond which no body can be compressed, is not inconsistent with Maxwell's statement. The hypothesis regards the ratio of the increment of strain to the increment of pressure as ultimately becoming infinitesimally small, but it in no way implies that this ratio ever becomes absolutely zero.

In a solid bar, supposed perfectly elastic, exposed to longitudinal stress, the ratio of the stress to the strain is styled Young's Modulus. In many materials Young's modulus varies in magnitude according to the direction in which the axis of the bar is taken. Thus, in ordinary woods, there is a marked difference between the value of Young's modulus in the direction of the pith of the tree and in any perpendicular direction. Materials in which Young's modulus is independent of the direction in which the axis of the experimental bar is taken are termed *isotropic*, all others are termed æolotropic.

In an isotropic elastic solid it is supposed, on the ordinary British or *biconstant* theory, that the value of Young's modulus, E, alone is insufficient to define the elastic structure, and that some other elastic constant must be known. For many purposes the most convenient additional constant is the ratio of the lateral contraction to the longitudinal extension—each measured per unit of length—in a bar exposed to simple longitudinal traction. For instance, if the diameter of a bar under uniform longitudinal stress change from 10 to 9·9997 inches the lateral contraction is ·00003, and if the longitudinal strain be ·0001, the ratio of lateral contraction to longitudinal extension is ·3. This ratio is termed Poisson's Ratio, and is represented here by η.

On the *uniconstant* theory of isotropy η must have the value ·25, which certainly accords well with experiments on glass and some of the more common metals, especially iron and steel under certain conditions.

On the biconstant theory η may have any value within

certain limits. The existence of these limits, it must be admitted, is seldom recognized, and experimental results are not infrequently referred to which are inconsistent with the view taken here, viz. that η must lie between 0 and ·5. If, however, η were negative in any material a circular bar of this material, when subjected to uniform longitudinal tension, would increase in diameter; while if η were greater than ·5, the bar, when fixed at one end and subjected to a torsional couple at the other, would twist in the opposite direction to the applied force. Until these phenomena are shown to present themselves in isotropic materials—and the experimental verification ought to be easy—it seems legitimate to suppose that when experimentalists deduce values for η which lie outside of these limits, their experiments refer to bodies whose constitution is different from what is assumed in their mathematical calculations.

The properties attributed to an isotropic elastic solid by the ordinary mathematical theory are as follows :—

(A) The strain must be elastic, *i.e.* it must disappear on the removal of the stress.

(B) The ratio of stress to strain must be independent of the magnitude of the stress, or, in Professor Pearson's words, the stress-strain relation must be *linear*.

(C) The strains must be small.

(D) The values of Young's modulus and Poisson's ratio in a bar of the material must be independent of the direction in which the axis of the bar is taken.

The last property alone distinguishes isotropic from æolotropic elastic solids.

(A) answers to Maxwell's definition, but (B) and (C) are not assumed by Maxwell. In other words, a solid may be perfectly elastic without showing a linear stress-strain relation, or possibly even after the strains have become large. Thus, for the sake of clearness, I shall call Maxwell's limit of perfect elasticity the Physical limit, and the limits supplied by (B) and (C) the first and second Mathematical limits respectively.

It is not infrequently taken for granted that the physical and the first mathematical limit are necessarily identical, *i.e.* that the elasticity is certainly not perfect when the stress-strain relation ceases to be linear. According, however, to some experimentalists cast iron is as perfectly elastic as any other metal in the sense of Maxwell's definition, but the stress-strain relation for even small strains is sensibly not linear*.

* See Todhunter and Pearson's 'History of Elasticity,' vol. i. art. [1411] and pp. 891–3.

This is of course a question for experimentalists to decide, but in any case where their final verdict is that the stress-strain relation is sensibly not linear the employment of the ordinary mathematical theory is unjustifiable. It must be admitted that the principle (C) is a very vague one, leading to no exact limit, and that it seldom receives any very formal acknowledgment. It is, however, clearly recognized, and a reason for it assigned in the following statement due to Thomson and Tait * :—"The mathematical theory of elastic solids imposes no restrictions on the magnitudes of the stresses, except in so far as that *mathematical necessity requires the strains to be small enough to admit of the principle of superposition.*" The italics are mine. The meaning is that the strains must be small fractions whose squares are negligible compared to themselves. If this principle be neglected and the mathematical equations be supposed to apply when the strains are large, the difficulty of giving them a consistent physical interpretation is very great if not wholly unsurmountable.

In most materials having any claim to be regarded as elastic solids, the stress-strain relation for most ordinary stress systems certainly ceases to be linear while the strains are still small. We shall thus in the meantime leave the condition (C) out of account, though we shall have to return to it in treating of the so-called "theories of rupture."

The existence of the properties (A), (B), (D), presupposed by the mathematical theory, is determined not solely by the chemical constitution of the body, but also by the treatment to which it has been subjected. Thus a freshly annealed copper wire may, when loaded for the first time, be far from satisfying conditions (A) or (B), and yet by the process of loading and unloading it may be brought into a *state of ease*, wherein these two conditions are very approximately, if not exactly fulfilled, so long as the stress does not exceed a certain limit. Again, the fact that a large mass of metal is sensibly isotropic is no sufficient reason for attributing isotropy to the same metal when rolled into thin plates or drawn into thin wires.

It is quite possible that the three conditions (A), (B), and (D) represent an ideal state which is never actually reached, and that a divergence may always be shown by the use of very delicate apparatus. If this be true, then the results obtained by the mathematical theory cannot claim absolute correctness. It seems, however, to be satisfactorily established

* Nat. Phil. vol. i. Part ii. p. 422.

that many materials in the state of ease satisfy these conditions with at least a very close approach to exactness, so that the results of the mathematical theory when properly restricted are then sufficiently exact for practical purposes.

From the preceding statements it will be seen that it is of the utmost importance to know what are the limits within which the conditions assumed by the mathematical theory are satisfied with sufficient exactness to justify its application. This question must of course be settled by experiment, but it is beset by various difficulties which ought to be clearly recognized. These arise in part from the serious obstacles in the way of a complete experimental knowledge, and in part from the want of a proper understanding between those interested in the practical and theoretical sides of the subject, and a consequent confusion in the terms used.

To avoid complication let us begin by supposing the mathematical limit of perfect elasticity to coincide with the physical. Let us consider the simple case of a bar under uniform longitudinal traction. We may suppose the bar isotropic, and in consequence of suitable treatment perfectly elastic for loads not exceeding L_1. No mechanical treatment, we shall suppose, can render it perfectly elastic for loads greater than L_2. It does not follow that a load L_2 will necessarily rupture the bar either immediately or in course of time, but simply that for any load greater than L_2 the strain is not perfectly elastic. Increasing the load from zero we should reach a load L_3, probably greater than L_2, that would in process of time rupture the bar, or a load L_4 greater than L_3 that produces immediate rupture. All these loads are supposed to refer to unit of area.

Now in the initial state of the bar we should be entitled to apply the mathematical theory only until the load L_1 was reached. When we aim at finding the utmost capability of the material under longitudinal load, we may perhaps apply the theory until the load L_2 is reached, but here we must stop. To apply it until the loads L_3 or L_4 are reached—assuming these greater than L_2—is clearly inadmissible.

Results of a similar kind hold for all the comparatively simple forms of stress,—such as pure compression, torsion, or bending—in which practical men are interested. There are limits to the state of perfect elasticity lower than the limits at which rupture takes place, at least immediately.

The usual aim of the engineer is that no part of the structure he is designing should ever be strained beyond the elastic limit, and this end he of course desires to obtain with the least possible expenditure of material. Thus ideally he

might be expected to calculate the dimensions of each piece, so that for the maximum load it is to be subjected to it shall just not pass beyond the limit of perfect elasticity. There are, however, in general agencies, such as wind pressure, dynamical action of a moving load, &c., whose effects are not very fully understood and whose magnitude cannot always be foreseen. Thus it is the custom to allow a wide margin for contingencies. Now the limit of perfect elasticity seems the natural quantity to employ in allowing for this margin, but the uncertainties attending its determination are such that it is customary to employ the breaking-load instead. The breaking-load for the particular kind of stress the member in question is to be exposed to is divided by some number, *e. g.* 4 or 5, called a *factor of safety*, and the dimensions of the member are calculated so that its estimated load shall not exceed the quotient of the breaking-load by the factor of safety. The engineer varies the factor of safety according to the nature of the load, and according to the confidence he possesses in the uniformity of the material and in the completeness of his knowledge as to the vicissitudes the structure is exposed to. It has thus come to pass that attention has been largely directed to the breaking-loads, and theories have been constructed which aim professedly at supplying a law for the *tendency to rupture*, under the most general stress-systems possible, of materials whose rupture-points have been found under the ordinary simple stress-systems employed in experiment.

There are only two such theories of rupture for isotropic materials that at present possess any general repute. To understand them the reader requires to know that for any stress-system there are at every point in an isotropic elastic material three *principal stresses* along three mutually orthogonal directions, and likewise three *principal strains*, whose directions coincide with those of the principal stresses. If an imaginary small cube of the material be taken at the point considered with its faces perpendicular respectively to the three principal stresses, then no tangential stresses act over these faces. In a bar under a uniformly distributed longitudinal stress L per unit of cross section, two of the principal stresses are everywhere zero, and the third is parallel to the axis and equals L. If E be Young's modulus, and η Poisson's ratio for the material, supposed isotropic and elastic, the greatest principal strain is everwhere L/E and its direction is parallel to the axis. The two remaining principal strains are each $-\eta L/E$, and they may be supposed to have for their directions any two mutually perpendicular lines in the cross section of the bar.

One of the theories referred to above is that when the algebraic difference between the greatest and least of the principal stresses at any point—a pressure being reckoned negative—attains a certain value, rupture will ensue at this point. Thus, if in descending order of magnitude the principal stresses at a point be T_1, T_2, T_3, then $T_1 - T_3$ is the *stress-difference** at this point, and the theory asserts that rupture will ultimately ensue if the stress-difference anywhere equals L_3, the load for ultimate rupture of a bar of the material by longitudinal traction; while if the stress-difference anywhere equals L_4, the load for immediate rupture by longitudinal traction, then immediate rupture will ensue.

The second theory, which is supported by the great authority of de Saint-Venant†, replaces the stress-difference of the first theory by the greatest strain. It thus asserts that the condition for rupture is found by equating the largest value found anywhere for the greatest strain to the longitudinal strain answering to longitudinal traction L_3, or to that answering to the traction L_4, according as the rupture is ultimate or immediate. This theory maintains that extension in some direction is necessary for rupture.

The two theories may, as in the case of pure longitudinal traction, lead to the same result; but in general they do not, so one at least of them must be wrong. When we examine the theories, still supposing the mathematical and physical limits of perfect elasticity the same, a very obvious difficulty‡ presents itself. It is assumed that the stress-difference and greatest strain are derived by the mathematical theory; but that theory applies only so long as the material is everywhere perfectly elastic, whereas rupture, at least when immediate, presents itself after the elastic limit has been passed. Thus if the application of the mathematical theory lead to values for the maximum stress-difference and greatest strain equal to the values of these quantities answering to rupture, at all events when immediate, the true conclusion would seem to be that the fundamental hypothesis on which the treatment proceeds, viz. that the material follows the laws assumed by the mathematical theory, has been shown to be incorrect. Nothing has been proved except that the elastic limit must be passed and that the mathematical theory does not apply.

The only logical way of interpreting the theories is to

* See Professor Darwin, Phil. Trans. 1882, pp. 220–1, &c.; also Thomson and Tait's Nat. Phil. vol. i. Part ii. p. 423.

† See Pearson's 'The Elastical Researches of Barré de Saint-Venant,' Arts. 5 (*c*), &c.

‡ *Ibid.* Arts. 4 (*γ*), 5 (*a*), &c.

suppose that the maximum stress-difference and greatest strain are to be compared not with the values that answer to rupture, but either with those that answer to the limit of perfect elasticity or with those derived by dividing the values answering to rupture by some factor of safety. This factor must then be large enough to prevent the limit of perfect elasticity being passed. Thus from either point of view we encounter a formidable difficulty, viz. the uncertainty of what is the limit of perfect elasticity.

We have supposed that a bar may be brought into a state in which it is perfectly elastic for longitudinal tractions not exceeding L_2. Answering to this we have L_2 for the stress-difference, and L_2/E for the greatest strain. Now if the two theories described above really apply to the limit of perfect elasticity, the one would seem to maintain that L_2 is the limiting value of the stress-difference, the other that L_2/E is the limiting value of the greatest strain for all possible stress-systems in material of the same kind as that in the bar. The complete experimental proof or disproof of such theories is not likely to be easy. Thus taking, for instance, the case of longitudinal traction, suppose it were shown that a certain method of treatment which raises the elastic limit for load parallel to the axis of a bar does not raise the elastic limit for longitudinal load in a bar whose length lay in the cross section of the original bar. This would only suffice to prove that the treatment adopted did not give a fixed elastic limit the same for all kinds of strain, it would leave the possibility of such a limit being obtained in some other way an open question.

In the preceding remarks the mathematical and physical limits of perfect elasticity have been supposed identical. When they differ, the mathematical limit is of course that which must be employed in determining the range of the mathematical theory. It will certainly not exceed the physical limit. I may add that, while for certain structures such as isolated boilers the physical limit may most nearly concern the practical engineer, in other structures, such as girder bridges, the stress-strain relation is assumed to be linear in designing the several parts, so that the first mathematical limit is then of the utmost practical importance.

In the previous discussion of the stress-difference and greatest strain theories, as settling the limits of application of the mathematical theory, it has been taken for granted that the condition (C) was safeguarded by them. Now in most ordinary systems of loading this is probably the case, but it is not always so. For instance, if we assume the mathe-

matical theory to hold, a solid isotropic sphere under a uniform surface-pressure shows none but negative strains, and the three principal stresses are everywhere equal. Thus the greatest strain is everywhere negative, and the stress-difference everywhere zero. This is true irrespective of the magnitude of the surface-pressure, and so, according to both theories, the stress-strain relation would be linear and the mathematical theory would apply, however large the pressure was. According to the theories, one might continue to employ mathematical formulæ which indicated a reduction of the sphere to one millionth of its original volume. It is obvious, however, that a reduction of the volume by even a tenth would produce strains which are probably far in excess of those admitted by the principle (C). In formulating an objection to the universal application of the theories, I have preferred to attack them on the side of the principle (C) so as to show clearly that the high authority of Thomson and Tait is on my side. The example considered raises, however, what seems to me at least an equally strong argument against the theories from the side of the principle (B). For we must remember that the stresses inside the material are determined by the intermolecular forces. Now, whatever molecules may be, and however they may act on one another, it seems incredible that the molecular forces should lead to one and the same stress-strain relation, however much the mean molecular distance may be reduced. The fact that Sir W. Thomson regards the existence of an irreducible minimum volume as possible may, I think, be taken as proof that he is opposed to the view that it is possible for the stress-strain relation to remain linear under such circumstances. It thus seems to me, on various grounds, that the inevitable conclusion is that while one or other of the two theories may, under ordinary circumstances, be sufficient to define the limits of the mathematical theory, the result must always be checked by reference to the condition (C), or, what comes to the same thing, we must give up the mathematical theory when the strains it indicates are such as would markedly alter the mean molecular distance.

I next proceed to discuss the possibility of the earth's possessing an elastic solid structure, deriving the necessary data from three papers published in the 'Transactions' of the Cambridge Philosophical Society. For brevity these will be referred to as (*a*)*, (*b*)†, and (*c*)‡.

* Vol. xiv. pp. 250–369.

† Vol. xiv. pp. 467–483.

‡ Vol. xv. pp. 1–36.

The strains due to the action of the sun and moon being comparatively insignificant, we need consider only the "centrifugal" forces due to the earth's diurnal rotation, and the gravitational forces due to the mutual attraction of its parts.

The data supplied by Geology do not enable us to formulate any likely theory as to a probable distribution of density and elasticity throughout the earth regarded as an elastic solid. All we know with certainty is that the surface strata are on an average considerably below the mean density, that they differ widely in character, many being markedly æolotropic, and that frequently they are far from horizontal. Thus, as our object is merely to consider what are the possibilities on the hypothesis of solidity, it will be best to make the hypothesis as simple as possible. Now, if the deviations from the earth's mean density and from an isotropic elastic structure were limited to the surface-strata, where alone we are certain of their existence, the effect of the "centrifugal" forces would be nearly the same as if these deviations did not exist; but the effect of the gravitational forces on the eccentricity of the surface may depend largely on the nature of the deviations. I thus propose to treat the problem in stages.

The first stage neglects entirely the gravitational forces and regards the earth as a slightly spheroidal body—which has departed from the spherical form in consequence of its rotation—of uniform density and of the same isotropic elastic structure throughout, rotating with uniform angular velocity ω about its polar axis.

Let a denote the mean radius, d the difference between the equatorial and polar semi-axes of the surface, E Young's modulus, and η Poisson's ratio for the material. Then the ratio $d : a$ is given for various values of η in the following Table *:—

TABLE I.

$\eta =$	0	·2	·25	·3	·4	·5
$\frac{d}{a} \div \frac{\omega \rho a^2}{E} =$	·286	·330	·341	·352	·373	·395

In the case of an originally spherical solid assuming the shape of the earth under rotation, it is of no practical importance whether we regard a as the radius of the original spherical surface, or as the mean radius under rotation, nor does it matter practically whether the density be supposed uniform previous to or during the rotation. There is, it is

* See (*a*) formula (5) p. 287; or (*c*) Tables III., V., and VI.

true, for all values of η except ·5, a slight increase in the volume *, and consequent diminution in the mean density accompanying the rotation, but for our present purpose this may be neglected.

The mathematical solution on which Table I. is based treats the spherical surface of radius a as that over which the conditions for a free surface are satisfied. Now some uncertainty may exist, depending on the physical interpretation put upon the mathematical equations, whether these surface conditions should be applied over what is the surface before the displacement—in this case the surface of the true sphere which it is assumed the earth would form if the rotation disappeared, —or over what is the surface during the rotation. This uncertainty might constitute a very serious difficulty if the deformations were supposed to be large—a contingency which may arise when the limitation (C) in the magnitude of the strains is neglected ; but in such problems as the present where the strains are, as we shall see presently, of the same order of magnitude as occur in ordinary engineering structures, it is of no material consequence. In the present case complete assurance on this point may be derived from figures 1 and 2, plate ii. of (*c*), which show the changes induced by rotation in the equatorial and polar semi-axes of spheroids of various shapes.

For given values of d, a, ω, and ρ, Table I. shows that E and η increase together. Giving ω the value it has for the earth, and assuming $\rho=5{\cdot}5$, $a=3950$, $d=13{\cdot}25$, I find for the values of E, measured in grammes weight per square centim., answering respectively to the values 0, ·25, and ·5 of η, the approximate numbers

$$1020\times10^6, \quad 1220\times10^6 \quad \text{and} \quad 1410\times10^6.$$

It is obvious from Table I. that to equal increments in η there correspond nearly equal increments in E ; thus the numbers given above will enable a sufficiently close approximation to the value of E for any other value of η to be immediately written down.

For the sake of comparison with the values found for E in some of the commoner materials under ordinary conditions I append the following data, taken from Sir W. Thomson's article on 'Elasticity' in the *Encyclopædia Britannica*. The units are the same as above.

* See (*b*) Table II., and compare Tables V. and VI. of (*c*).

TABLE II.

Values of $E/10^6$.

	Iron and Steel.	Copper.	Slate.	Zinc.	Stone.	Lead.
Highest value .	2953	1254	1120	955	about 350	199
Lowest value...	984	1052	910	873		51

This table will give a general idea of the limits within which E may reasonably be expected to lie, though some of the data refer to material which is hardly likely to have been isotropic. It shows that if the influence of the gravitational forces on the eccentricity were negligible—which, however, is not the case—the earth, though perfectly solid and elastic, might reasonably be expected to display not a smaller but a considerably greater eccentricity than it actually does.

The question next arises whether the strains and stresses produced by the rotation are such as are consistent with the principles on which the application of the mathematical theory rests. In the actual case of the earth this question is of importance only in exceptional circumstances, owing to the preponderating influence of the gravitational forces, still it possesses sufficient interest to claim separate consideration. The following table gives a sufficiently close approximation to the numerical results obtained for the rotating body treated above, when for E are substituted the values which answer to the production by rotation alone of an eccentricity equal to that of the earth.

TABLE III.*

$\eta=$	0	·25	·5
Maximum stress-difference in tons weight per square inch	32¾	32¼	32
Greatest strain	·0040	·0029	·0018
Longitudinal stress in tons per square inch which would produce a strain equal to the greatest strain.....	26	23	16

* See (*c*) Tables III., VII., and IX.

The maximum stress-difference and the greatest strain, as given in the table, are both found at the centre.

The result on the stress-difference theory is nearly independent of η, and is more unfavourable in every case than that given by the greatest strain theory to the view that the material remains perfectly elastic. A stress of 16 tons per square inch is not one that an engineer would view with complacency in any structure intended to be permanent, but it is a low value for the tenacity of good wrought iron. A stress of even 33 tons per square inch can easily be borne without rupture by good steel, and is perhaps not in excess of the stress under which the best steel remains practically perfectly elastic. The greatest strains are not of such a magnitude as to raise any presumption against the linearity of the stress-strain relation. Thus, according to all the tests, it is quite possible that an originally spherical solid of the earth's mass but devoid of gravitation should remain solid and elastic while assuming the form of the earth under rotation. Its material, however, at least if homogeneous and isotropic, would require to possess an unusually high limit of perfect elasticity.

The next subject for consideration is how the question is affected by the existence of gravitational forces such as are found in the case of the earth. The strains and stresses in a slightly oblate spheroid, treated as an isotropic elastic solid, all consist of two parts, the first part being the same as if the surface were truly spherical, the second depending on the eccentricity. It is the second parts that represent the action of the gravitational forces in modifying the eccentricity, but these parts are in general insignificant so far as the question of the applicability of the mathematical theory is concerned. I shall therefore postpone consideration of them until an account has been given of the strains and stresses which are independent of the eccentricity.

The mathematical difficulties in applying the ordinary theory to the case of a homogeneous solid gravitating sphere are trifling, but the difficulty of putting a physical interpretation upon the mathematical expressions answering to most values of η is such as very forcibly to call attention to the necessity of the limitation (C). Since the gravitational force at an element of a solid sphere depends not only on the total mass which lies nearer the centre than does the element, but also on its absolute distance from the centre, we must assume that the equations supplied by the ordinary mathematical theory, if they apply at all, hold for the position of final equilibrium after the deformations have taken place. This

seemingly requires that strain should be defined as the ratio of the increase of length to the final length, which is not in accordance with the usual interpretation of Hooke's law unless the square of the strain be negligible. Supposing the internal equations to refer to the final deformed condition, the surface equations will undoubtedly also refer to this condition. Thus, so far as the terms independent of the eccentricity are concerned, we may suppose the mathematical theory applied to a sphere whose density ρ is uniform throughout, and whose radius a equals the earth's mean radius.

In this case the maximum stress-difference and the algebraically greatest strain are both found at the surface. Let us denote these by $\bar{\mathrm{S}}$ and $\bar{s}$ respectively; and let s_0 denote the greatest compression, which occurs at the centre, and u_a the radial displacement at the surface. Employing E and η as before, and denoting by g the acceleration due to the sphere's attraction at its surface, I find*

$$\bar{\mathrm{S}} = \frac{1}{5} g\rho a \frac{1-2\eta}{1-\eta}, \quad \ldots \ldots \ldots \quad (1)$$

$$\bar{s} = \frac{2}{5} \frac{g\rho a}{\mathrm{E}} \frac{\eta(1-2\eta)}{1-\eta}, \quad \ldots \ldots \ldots \quad (2)$$

$$s_0 = -\frac{3}{10} \frac{g\rho a}{\mathrm{E}} \frac{(1-2\eta)(1-\eta/3)}{1-\eta}, \quad \ldots \quad (3)$$

$$u_a = -\frac{1}{5} \frac{g\rho a^2}{\mathrm{E}} (1-2\eta). \quad \ldots \ldots \ldots \quad (4)$$

Assuming for a moment these results to hold for a sphere in which g = gravity† at the earth's surface, $\rho = 5{\cdot}5$ times the density of water, and $a = 3950$ miles, the following are the approximate numerical values answering to the values 0, ·25, and ·5 of η :—

TABLE IV.

$\eta =$	0	·25	·5
S, in tons weight per square inch	4440	2960	0
Longitudinal stress $\mathrm{E}\bar{s}$, in tons weight per square inch, which would produce a strain $\bar{s}$	0	1480	0
$-s_0$ (see below)	1·03	·53	0
$-u_a$, in miles (see below)	2700	1130	0

* See (*a*) formulæ (17), (18a), and (19a), p. 281.

† The calculations treat the attraction on a cubic centimetre of water at the surface as equal to the weight of one gramme. In reality of course "gravity" includes the "centrifugal" force.

For a given value of η the value of $\bar{S}$ is independent of E. It diminishes continually as η increases from zero. Since the value of $\bar{s}$ depends on E, I have given the value of $E\bar{s}$, or the longitudinal stress which would produce in a bar of the material a strain equal $\bar{s}$. The value of $E\bar{s}$ has a maximum of about 1520 tons weight per square inch, for $\eta = 1 - \sqrt{1/2}$ or ·293 nearly.

For $\eta = \cdot 5$ the values of s_0 and v_a are zero supposing E finite, but for other values of η one can obtain numerical measures of these quantities only by assigning numerical values to E. Now if the earth were an elastic solid truly spherical but for its rotation, the value of E answering to a given value of η would be determined from the eccentricity of the surface. But the action of the gravitational forces, as will be seen more clearly presently, largely reduces the eccentricity which rotation would produce in a sphere of given material. Thus the eccentricity varying inversely as E, the value of E answering to a given eccentricity is necessarily considerably smaller when gravitational forces act along with the "centrifugal" than when the latter act alone. Since the surface-strata are very variable and of much smaller mean density than the earth as a whole, any calculation of the reduction of our estimates of E, when gravitational forces are allowed for, which treats the earth as of uniform density cannot lay claim to great accuracy. For this reason, and also because I am specially desirous not to overstate the case against the application of the mathematical theory, I have in calculating the values of s_0 and u_a in Table IV. ascribed to E the values it would possess in the total absence of gravitational forces, viz. the values 1020×10^6 for $\eta = 0$ and 1220×10^6 for $\eta = \cdot 25$ in the same units as before. The numerical values ascribed to s_0 and u_a in the table are thus essentially minima, which would in reality have to be increased probably to a considerable extent.

It will be seen from the formulæ and from Table IV. that when η is zero or is small, the application of the mathematical theory would be fully justified on the greatest strain theory, while utterly condemned on the stress-difference theory. The principle (C) is in this case entirely in agreement with the stress-difference theory, and the application of the mathematical theory can in fact be supported only by those who reject this principle, and consider it possible for the stress-strain relation to remain linear though a solid sphere is reduced to one fourth or less of its original volume.

Noticing from (1) and (2) that $E\bar{s}/\bar{S} = 2\eta$, we see that for

all values of η less than ·5 the stress-difference theory is less favourable to the view that the mathematical theory is applicable than the greatest strain theory. If there is any truth in either theory, the earth's material cannot possibly possess a linear stress-strain relation for values of η such as ·25 (*i. e.* with a structure such as that of the metals) unless it be of a strength compared to which that of steel is insignificant. For such values of η the strains are also enormously in excess of those which can be admitted according to the principle (C).

When, however, η approaches the limiting value ·5 a complete change comes over the features of the case. The maximum stress-difference and all the strains diminish, eventually vanishing when $\eta = ·5$. Thus none of the objections hitherto encountered can be urged against the application of the mathematical theory when η equals or nearly equals ·5. To the exact value ·5 of η there is, I admit, a physical objection, which would doubtless have been urged by Maxwell, viz. that, supposing Young's modulus to be finite, this implies the material to be absolutely incompressible. There is, however, no obvious physical objection to the hypothesis that the material is very nearly incompressible, *i. e.* that $·5 - \eta$ is very small*; and an isotropic sphere with such a structure would, according to all our tests, remain perfectly elastic when possessed of the earth's mass and exposed to its gravitational forces.

In our previous estimate of the value of E the action of the gravitational forces in reducing the eccentricity was not taken into account. If the principles we have laid down as regulating the applicability of the mathematical theory be conceded, we need only consider the case when $·5 - \eta$ is very small; and since the formulæ show that in this case a small variation in the value of η is of little consequence, we may for simplicity suppose $\eta = ·5$ exactly.

In order to show the nature of the uncertainty that must in reality be attached to the result, it seems desirable to give a general idea of the way in which the existence of gravitational forces affects the eccentricity. Let us imagine, then, that over the surface of a perfect sphere weightless matter is piled up, which transforms the surface into that of a slightly oblate spheroid whose polar and equatorial semi-axes are respectively $a - 2d/3$ and $a + d/3$. Now suppose the heaped-up material to become heavy. The pressure it exerts on the surface below it is greatest in the equator and is zero at the

* Stewart and Gee, in their 'Elementary Practical Physics,' vol i. pp. 192–5, give data from which they conclude that india-rubber is such a material.

poles. Thus the originally spherical surface will tend to sink at the equator and to rise at the poles; consequently the difference d between the equatorial and polar semi-axes of the spheroidal surface will diminish, but the diminution is clearly less the smaller the density of the heaped-up material.

It must be understood that this does not profess to be a complete account of what actually happens; but it may suffice to show that the gravitational forces tend to reduce the eccentricity which the centrifugal forces tend to develop, and also that this reduction may depend largely on the density of the surface layers. If the departure of the surface layers from the earth's mean density occurs mainly near the equator, then the action of the gravitational forces in reducing the eccentricity may be much less than it would seem to be on the hypothesis of an earth of uniform density.

Treating the density as uniform and η as equal ·5, I find that, for a given value of E, the existence of the gravitational forces would in such a case as that of the earth reduce the difference between the equatorial and polar diameters called for by the rotation in the ratio of 9 : 40 approximately*. Thus, for a given eccentricity, the value of E when the gravitational forces act is to its value when the centrifugal forces alone exist as 9 : 40. So in the supposed case of the earth, we should have to reduce E from 141×10^7 to 32×10^7 grammes weight per square centim. The maximum stress-difference reduces to 7·2 tons weight per square inch. The greatest strain remains ·0018, as before, but it would answer to a purely longitudinal stress of only 3·6 tons per square inch. Owing to the less density of the surface-strata these reductions may be considerably too great, so that it is advisable to regard 32×10^7 as essentially a lower limit to the value of E. As stated above, the numerical result for the value of E would be but little altered if we supposed η slightly less than ·5; but unless $\cdot 5 - \eta$ be very small, the terms independent of the eccentricity become of importance in estimating the maximum stress-difference and greatest strain.

The conclusion to which the previous investigations lead is, that none of the principles at present recognized in the biconstant theory of isotropy are opposed to the hypothesis that the earth possesses in its interior an isotropic elastic solid structure with a linear stress-strain relation, provided its material be very nearly incompressible. But the hypothesis that the material in the interior shows an isotropic elastic structure, such as that of the ordinary metals under the ordinary conditions to which they are exposed on the earth's

* *Cf.* (*a*) formula (21), p. 283, and (5), p. 287.

surface, can be maintained only by those who are prepared to reject the usual theories of the rupture, the limitation (C) in the size of the strains, and the argument introduced here from the theory of intermolecular forces. This raises no presumption against the hypothesis that the interior is in a perfectly solid state, and possessed of such a chemical constitution, say, as iron, if it be admitted that it is of a material in which the linearity of the stress-strain relation ceases when the compression becomes large.

The results obtained raise no presumption for or against the theory that the earth is in a liquid or plastic state. They merely show that any argument against the possibility of an elastic solid structure in a body of the earth's *form* is without foundation ; and that any argument based on the destructive tendency of the enormous gravitational forces in a solid of its mass is inconclusive, even as directed against such structures as are compassed by the ordinary mathematical theory. It has not been shown that an æolotropic solid structure of some kind, or of a variety of kinds, may not satisfy all the conditions as well as or even better than a nearly incompressible isotropic material. The presumption is, in fact, that the conditions may be satisfied in an infinite number of ways.

It must be borne in mind that there may be fatal objections to an elastic solid structure which do not arise immediately from the theory of elasticity. Such an objection may arise from the rapid increase with the depth shown by the temperature near the earth's surface. My principal reason for referring to this is to point out that the common argument against the production of fluidity by the high internal temperature (viz. an assumed raising of the melting-point by pressure) has just as much weight for a nearly incompressible solid earth as for any other, because while the stress-difference in such an earth is small the internal pressures are extremely large.

Before passing to the second part of the paper, I have to confess that there is no reason to believe that some of the limitations assigned here to the application of the mathematical theory will be accepted by all or even by a majority of elasticians. In fact the mathematical theory has actually been applied by several recent writers under circumstances when most or all of the limitations proposed here are violated. For instance, this is to a certain extent the case in Professor Darwin's paper*, "On the Stresses caused in the Interior of the Earth by the Weight of Continents and Mountains." In the principal part of the paper he supposes $\eta = \cdot 5$, when, as we

* Phil. Trans. 1882, pp. 187–230.

have seen, none of the objections apply; but in his § 10, in order "to know how far the results . . . . may differ, if the elastic solid be compressible," he supposes that while the rigidity constant is finite the bulk modulus is very small. In other words, he applies mathematical formulæ which assume η nearly equal to -1. Such a value has been here regarded as impossible. It should also be noticed that if η were equal -1 then E would vanish, and if η be nearly -1 the value of E must be very small. Thus the strains and displacements given by equations (2) to (4) would in the case supposed by Professor Darwin be enormously greater than even those given in Table IV. I do not observe, however, that either in the paper itself or in one supplementary* to it Professor Darwin makes any explicit reference to the terms in the strain independent of the angular coordinates, from which the equations (1) to (4) are derived. I am thus unable to say whether his neglect of the limitations that these terms are here regarded as setting to the application of the mathematical theory is intentional or not. Again, in a recent paper†, "On Sir William Thomson's estimate of the Rigidity of the Earth," Mr. Love has also considered the problem of the earth treated as an isotropic elastic sphere, more especially for the value ·25 of η. In his equations (14) and (18) Mr. Love determines the values of two arbitrary constants which occur in the terms independent of the angular coordinates; and it is easily seen that the expression he would thence obtain for these terms is identical with mine‡. After determining the second constant he, however, dismisses the subject with the remark, "This . . . . gives the mean radial displacement, a matter which need not detain us here." So far as I can see, Mr. Love makes no reference to any principle such as (C), nor to the possibility of the stress-strain relation ceasing to be linear.

I ought also to explain that in my paper (*a*), directing my attention solely to the theories of rupture, I left out of sight any such limitation as (B) or (C), and treated the case of an earth in which $\eta = 0$ as one in which, according to the greatest-strain theory of rupture, the mathematical theory was applicable. I also failed to notice that the case $\eta = \cdot 5$ was sanctioned by the greatest-strain theory as well as by the stress-difference theory.

[To be continued.]

* Proceedings of the Royal Society, vol. xxxviii. (1885), pp. 322–8.

† Trans. Camb. Phil. Soc. vol. xv. pp. 107–118.

‡ (*a*), equation (17), p. 281.

XXXIV. *The Theory of Magnetism and the Absurdity of Diamagnetic Polarity.* *By* J. PARKER, *M.A., Fellow of St. John's College, Cambridge.*

[Continued from p. 203.]

IT appears from experiment that the properties of exerting actions at a distance by a magnet are mainly situated at or near the ends of the magnet. Suppose, then, that we have two long magnets A, B, which may be considered to possess the magnetic properties only in their ends, and let these magnets be so placed that we need only take into account one end of each. Also let these two ends be so far from each other that they may be regarded as mathematical points P, Q. Then the only magnetic forces between the two magnets will be equal forces at the poles P, Q, acting along the line PQ in opposite directions.

Now let the two magnets be situated in a "vacuum" and be made to undergo a reversible cycle in which the velocities are constantly zero. To do this, they must be held by external forces equal and opposite to gravity and to the magnetic forces between P and Q. But if the equal forces between P and Q be denoted by F, a repulsion being considered positive and an attraction negative, the work done by F in a small change of the distance PQ ($=r$) will be $F\,dr$. Hence the work done on the system during the cycle by the *external* forces is $-\int F\,dr$, where the two limits are identical. This must be zero, by the principles of thermodynamics, and therefore F must depend only on r, or $F=f(r)$. From experiment it appears that $f(r)$ is proportional to $\frac{1}{r^2}$, so that if the force between P and Q when their distance is one centimetre be λ dynes, the force will be $\frac{\lambda}{r^2}$ dynes when the distance is r centimetres.

Now let there be any number of poles R, R′, R″, . . . , which may be treated as mathematical points, acted on simultaneously by P and Q. Then it is inferred from experiment, supported by theory, that if the two poles P, Q repel each other, the forces they exert on any one of the other poles, R, will be both repulsive or both attractive; but that if P and Q attract each other, the forces they exert on any one of the other poles will be one repulsive and the other attractive. Conversely, if P and Q both repel or both attract the pole R, they will repel each other; while if one attract and

the other repel, they will attract each other; and the very same properties are true of all the poles.

Thus it appears that there are two kinds of poles, or of magnetism. Like kinds repel; unlike kinds attract. For instance, if P and Q repel each other, they are of the same kind. If both P and Q repel a third pole R, R will be of the same kind as P and Q; if both P and Q attract R, it will be of unlike kind to P and Q.

The two kinds of magnetism may be distinguished by the signs + and −. It is immaterial which kind of magnetism be considered positive; but it is generally agreed to take the kind found at that end of a soft bar of iron which, when freely suspended and in stable equilibrium, points to the north.

If the poles P, Q exert equal forces, both attractive or both repulsive, on any third pole R from which they are equally distant, the poles P, Q, or the quantities of magnetism at P and Q are said to be equal. If the forces be equal, but one attractive and the other repulsive, the poles P, Q are said to be equal and opposite, or the quantities of magnetism at P and Q are said to be numerically equal but of opposite sign. Again, if the pole P exert m times as great a force as Q, and both be attractive or both repulsive, the magnetism at P is said to be $+m$ times that at Q. If one force be attractive and the other repulsive, the magnetism at P is said to be $-m$ times that at Q. Lastly, it is inferred from experiment, supported by theory, that if two poles X, Y be at the same distance as two equal poles P, Q, and the magnetism at X be x times that at P, and that at Y y times that at Q, the force between X and Y will be xy times that between P and Q. The force between X and Y is repulsive if X and Y, or x and y, be of the same sign, that is, if the product xy be positive: the force is attractive if x and y be of opposite signs, or xy negative.

These results lead to the C.G.S. system of units. If two equal positive poles P, Q, situated at a distance of one centimetre, repel each other with a force of one dyne, the quantity of magnetism at P or Q is defined to be the unit of magnetism. It therefore follows that if two poles X, Y, at which the quantities of magnetism are m and m', be at a distance of r centimetres, the magnetic force between them will be $\frac{mm'}{r^2}$ dynes, repulsive forces being considered positive and attractive negative.

To complete the fundamental principles of magnetism, we must add the great principle of the Conservation of Magne-

tism, which asserts that whatever changes take place in the magnetization of a system, the quantity of magnetism remains constant.

In the ordinary text-books, the fundamental definitions &c. are given in a manner which we cannot accept. Thus, let A, B be two long magnets which may be supposed to possess the magnetic properties only in their ends, and let them be so placed that we need only consider the positive pole of each, viz., P on A and Q on B. Then, if these poles are equal, and if, when they are placed "in air" at a distance of one centimetre, a force of one dyne is required to overcome the force which tends to separate them, the strength of each pole is defined to be unity, and it is asserted that at a distance of r centimetres "in air," the force which tends to separate them is $\frac{1}{r^2}$ dynes. In our method of treating the subject, we should say that the force which tends to separate the two poles is partly due to the magnetisms of the poles themselves, partly to the magnetization of the air in which the two magnets are placed, and partly to the inequalities in the pressure of the air. In some experiments, the pressure of the air is the most important factor. The so-called definitions of the text-books are therefore not definitions at all, but propositions in the Kinetic Theory of Gases, and are possibly incorrect.

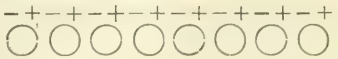
Having now explained the fundamental principles of the subject, we must consider how magnetism is distributed in bodies. In the first place, it is evident that a finite quantity of magnetism cannot be concentrated into a point—that is into an indefinitely small sphere; for any two parts of the sphere would exert very great forces on each other, and the sphere would fly to pieces.

A finite quantity of magnetism can be distributed on a finite area. For if σ be the quantity of magnetism per unit area, or the surface density, on an infinite plate, this plate will exert a magnetic force $2\pi\sigma m$ on a body P with a quantity of magnetism m. If P be a second plate on which the surface-density is σ', the force exerted by the infinite plate on each unit of area of P will always have the finite value $2\pi\sigma\sigma'$.

If we break a magnet into any number of pieces, each piece is found to be a complete magnet. From this it is inferred that each atom or molecule is a complete magnet with equal quantities of positive and negative magnetism at its ends. The total quantity of magnetism on each atom or molecule is therefore zero, and the distribution on it may be supposed to be a surface distribution. To prevent any difficulty being felt with respect to surface distributions of

magnetism, we have only to mention that, according to the physical theories of magnetism, all that is meant is a finite pressure or tension per unit area on the surface.

The reason why, in an ordinary bar-magnet, there is little manifestation of the magnetic properties except near the ends, is supposed to be that the positive end of one atom or molecule and the negative end of the next partially neutralize one another,

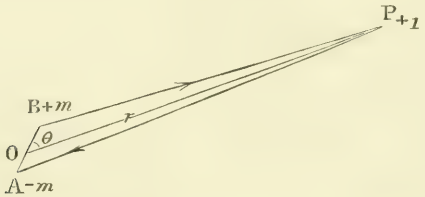


as indicated by the figure.

To calculate to what extent the magnetisms of successive molecules neutralize one another, we require some preliminary propositions.

Suppose that a very short, thin, straight magnet of length l is placed with its centre at O and let the quantities of magnetism at its two ends A, B, which may be treated as mere

Fig. 6.



points, be $-m$ and $+m$. Let a unit positive pole be situated at a point P whose distance from O is r, and let θ be the angle between OP and the line AB, or the axis of the magnet. Then the magnet AB exerts on P a repulsive force $\frac{m}{PB^2}$ along BP and an attraction $\frac{m}{PA^2}$ along PA. Now $\frac{m}{PB^2}$ along BP is equivalent to $\frac{m}{PB^2}\frac{OB}{PB}$ parallel to BA and $\frac{m}{PB^2} \times \frac{PO}{PB}$ parallel to OP; and $\frac{m}{PA^2}$ along PA is equivalent to $\frac{PA^2}{m} \times \frac{AO}{PA}$ parallel to BA and $\frac{m}{PA^2}\frac{PO}{PA}$ parallel to PO. Hence the action of the elementary magnet AB on P is equivalent to a force $\frac{ml}{2}\left(\frac{1}{PB^3}+\frac{1}{PA^3}\right)$ acting at P parallel to BA and a force $m\,PO\left(\frac{1}{PB^3}-\frac{1}{PA^3}\right)$ at P along OP.

But, if we retain only the most important terms,

$$\frac{ml}{2}\left(\frac{1}{\mathrm{PB}^3}+\frac{1}{\mathrm{PA}^3}\right)=\frac{ml}{2}\left\{\frac{1}{\left(r-\frac{l}{2}\cos\theta\right)^3}+\frac{1}{\left(r+\frac{l}{2}\cos\theta\right)^3}\right\}$$

$$=\frac{mlr^3}{\left(r^2-\frac{l^2}{4}\cos^2\theta\right)^3},$$

$$m\,\mathrm{PO}\left(\frac{1}{\mathrm{PB}^3}-\frac{1}{\mathrm{PA}^3}\right)=mr\left\{\frac{1}{\left(r-\frac{l}{2}\cos\theta\right)^3}-\frac{1}{\left(r+\frac{l}{2}\cos\theta\right)^3}\right\}$$

$$=\frac{3mlr^3}{\left(r^2-\frac{l^2}{4}\cos^2\theta\right)^3}\cos\theta.$$

Thus if we can neglect $\frac{l^2}{r^2}$, as we certainly can when AB is comparable to the size of a molecule, the action on P reduces to $\frac{ml}{r^3}$ parallel to BA and $\frac{3ml}{r^3}\cos\theta$ along OP. These forces are exactly the same as would have been produced by another short magnet similar to AB, placed along AB with its centre at O, provided that $m'l'=ml$. Defining ml to be the magnetic moment of the elementary magnet AB, we see that two elementary magnets placed at the same point O with their axes coincident are equivalent to each other if their moments are equal.

If we take three rectangular axes Ox, Oy, Oz through O and denote the coordinates of P by (x, y, z) and the angles AB makes with the axes by (α, β, γ), the forces exerted on P by three small magnets placed at O :—

$ml\cos\alpha$ along Ox, are $-\frac{ml}{r^3}\cos\alpha$ parallel to Ox and $\frac{3ml\cos\alpha}{r^3}\frac{x}{r}$ along OP ;

$ml\cos\beta$ along Oy, are $-\frac{ml}{r^3}\cos\beta$ parallel to Oy and $\frac{3ml\cos\beta}{r^3}\frac{y}{r}$ along OP ;

$ml\cos\gamma$ along Oz, are $-\frac{ml}{r^3}\cos\gamma$ parallel to Oz and

$$\frac{3ml\cos\gamma}{r^3}\frac{z}{r} \text{ along OP.}$$

These forces combined give $\frac{ml}{r^3}$ parallel to BA and

$$\frac{3ml}{r^3}\left(\frac{x}{r}\cos\alpha+\frac{y}{r}\cos\beta+\frac{z}{r}\cos\gamma\right),$$

or $\frac{3ml}{r^3}\cos\theta$, along OP. We may therefore say that the action of a small magnet AB is equal to the sum of the actions of its components.

A molecule may be supposed made up of several elementary magnets such as AB. As each of these constituent elementary magnets is equivalent to three component magnets parallel respectively to the three rectangular axes, the whole molecule is equivalent to three elementary magnets parallel respectively to the axes, and therefore equivalent to a single resultant elementary magnet. The magnetic moment and direction of this resultant magnet may be called the magnetic moment and axis of the molecule.

As neighbouring molecules may be magnetized differently, we shall avoid the irregularities by considering a volume dv which, though very small, is still large enough to contain many molecules. Since each molecule in the volume is equivalent to three small component magnets parallel to the axes, the whole volume dv is equivalent to three small component magnets, and therefore to a single small magnet. If we denote the moment of this single magnet by $I\,dv$, I is defined to be the intensity of magnetization of the element, or at a point in the element, and the direction of I is defined to be the direction of magnetization.

If A, B, C be the components of I parallel to the axes, it is evident that the external action of the element dv is equal to the sum of the actions of three equal volumes placed successively in the same position, whose magnetizations are respectively parallel to the axes and equal to A, B, and C.

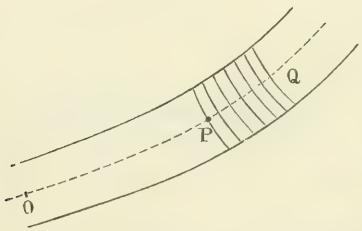
If we draw a curve such that the tangent at any point is the direction of magnetization at that point, the curve may be called a line of magnetization. It is generally continuous so long as we keep to the same body. If at any point two consecutive tangents cut at a finite angle, we shall consider, that.

for magnetic purposes, we enter a new body when we travel along the line of magnetization past the point at which the discontinuity takes place.

If the elementary volume dv be in the form of a cylinder, of small length and thickness, whose generators are lines of magnetization and whose ends are orthogonal sections, it is evident, from what has been shown, that the external magnetic action of the volume is the same as that of layers of magnetism on the ends, of surface-densities I on the positive end and $-\mathrm{I}$ on the negative end.

We shall now suppose the body divided into a vast number of elementary cylinders such as these, and we shall examine how far the magnetic layers on contiguous ends neutralize one another. Let O be a fixed point on a line of magnetization and P, Q two other points, such that the distance $\mathrm{OP}=s$ and $\mathrm{OQ}=s+ds$. Round the line OPQ describe a small closed curve and let a line of magnetization travel round it so as to trace out a thin tube in the body. Through P and Q draw

Fig. 7.

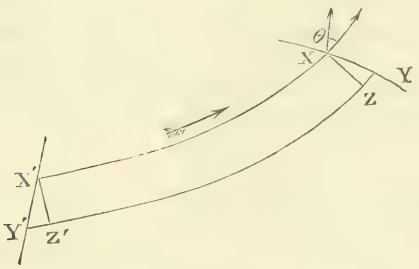


normal surfaces to the line OPQ, and let $d\alpha$ be the area of the section of the tube at P or Q. Then let the length PQ be divided into an infinite number of equal parts, each of which may be supposed considerable in comparison with the size of a molecule, and through each of the points of division draw surfaces normal to PQ, so as to divide the small cylinder PQ into an infinite number of infinitely thinner cylinders. Then, since each of these constituent cylinders of PQ is equivalent to equal surface-layers on its ends, the densities of which vary uniformly from I at P to $\mathrm{I}+\frac{d\mathrm{I}}{ds}ds$ at Q, it is clear that the cylinder PQ is equivalent to layers on its ends, of surface-densities $-\mathrm{I}$ at P and $\mathrm{I}+\frac{d\mathrm{I}}{ds}ds$ at Q, together with a quantity of magnetism $-\frac{d\mathrm{I}}{ds}ds\,d\alpha$ uniformly distributed

throughout its volume. The density of the volume distribution is therefore $-\frac{dI}{ds}$, where the differential coefficient is found on a line of magnetization.

Now let a finite body be divided into an infinite number of thin tubes such as that surrounding the curve OPQ. Let one of these tubes meet the surface of the body in the curves XY, X′Y′, and draw two normal sections XZ, X′Z′ to the tube, entirely within the tube and just touching the curves XY, X′Y′ at the points X, X′. Then, when the section of the tube is indefinitely diminished, the external magnetic action

Fig. 8.



of XYY′X′ is ultimately the same as that of XZZ′X′, and is therefore equivalent to a volume-density whose value ρ at any point is $-\frac{dI}{ds}$, and a layer of surface-density I_X on XZ and another layer $-I_{X'}$ on X′Z′. Consider the section XZ. The layer on this section is equivalent to an equal quantity of magnetism distributed uniformly on the neighbouring small area XY. But if θ_X be the angle between the direction of magnetization and the outward drawn normal at X, the area XY = the area XZ × sec θ_X. The surface-density on XY is therefore $I_X \cos\theta$. Similarly the density on X′Y′ is $I_{X'} \cos\theta_{X'}$. Hence we arrive at the simple result, generally obscured or made mysterious by formidable integrations, that a finite body is magnetically equivalent to a volume distribution whose density ρ at any point is $-\frac{dI}{ds}$, together with a surface-layer whose value σ at any point of the surface is I cos θ, where θ is the angle between the direction of magnetization and the outward drawn normal at the point.

The expression for ρ can be put in a more convenient form. For if three equal bodies whose magnetizations are respec-

tively parallel to the axes and equal to A, B, C, be placed successively in the same position as the given body, the sum of their actions will be equal to that of the given body. Hence, since the body whose magnetization is parallel to Ox is equivalent to a volume distribution $-\frac{dA}{dx}$ and a surface-layer whose density at a point P where the outward drawn normal makes angles (λ, μ, ν) with the axes, is $A\cos\lambda$, we obtain

$$\rho = -\left(\frac{dA}{dx} + \frac{dB}{dy} + \frac{dC}{dz}\right),$$

and

$$\sigma = A\cos\lambda + B\cos\mu + C\cos\nu,$$

or, if the direction of magnetization make angles (α, β, γ) with the axes,

$$\begin{aligned}\sigma &= I(\cos\alpha\cos\lambda + \cos\beta\cos\mu + \cos\gamma\cos\nu)\\ &= I\cos\theta,\end{aligned}$$

as before.

We may now find the energy U and the entropy ϕ of any magnetized system at rest, with its magnetization in equilibrium, stable or unstable. For this purpose we shall first obtain the energy U′ and the entropy ϕ' of a magnetized system identical with the given system except that it is broken up into an infinite number of small pieces.

Without altering the internal conditions or the magnetic distribution of any part of the system (U', ϕ'), let all its elementary portions be removed to infinite distances from one another, and left without velocity. Suppose that in thus preventing the forces acting between the various elements from producing velocities, the work obtained from the system is $Y + W$, where the part Y is due to the magnetization of the system and W to gravitation. Then, since the operation is clearly reversible and unattended by any thermal phenomenon, the energy will now be $U' - Y - W$, and the entropy ϕ'. Also, since the values of the energy before and after the operation $(U', U' - Y - W)$ depend only on the two states, it is clear that $Y + W$, and therefore Y alone, is independent of the manner in which the change of state is effected.

Let us now consider one of the elements after it has been removed to an infinite distance from all the other elements. Its energy will be proportional to its volume dv, if that volume is small enough; and, if the substance be homogeneous (that is non-crystalline), will be independent of the angle the direction of magnetization makes with any line

fixed in the element. If, therefore, the element be homogeneous, and we suppose, for simplicity, that its state depends only on the intensity of magnetization I and the absolute temperature θ, the energy of the element may be written $F(I, \theta)dv$. Calling C the value of $F(I, \theta)$ when $I=0$, which is clearly finite, we may put $F(I, \theta)dv$ in the form $Cdv+\{F(I, \theta)-C\}dv$, or $Cdv+f(I, \theta)dv$, where $f(I, \theta)=0$ when $I=0$. We have then

$$U'-Y-W=\int Cdv+\int f(I, \theta)dv,$$

or

$$U'=Y+W+\int Cdv+\int f(I, \theta)dv.$$

Now if U_0' be the value of U' when the system (in its original state) is deprived of its magnetization, but otherwise unchanged, we shall have, since both Y and $\int f(I, \theta)dv$ vanish when $I=0$ and W does not alter,

$$U_0'=W+\int Cdv.$$

Hence

$$U'=U_0'+Y+\int f(I, \theta)dv.$$

If, therefore, we assume that $U'-U_0'$ is the same as if the system was not broken up, or equal to $U-U_0$, we obtain

$$U=U_0+Y+\int f(I, \theta)dv. \quad . \quad . \quad . \quad . \quad (1)$$

Similarly we may obtain

$$\phi'=\int Ddv+\int h(I, \theta)dv,$$

$$\phi_0'=\int Ddv,$$

and therefore

$$\phi'=\phi_0'+\int h(I, \theta)dv,$$

from which we may infer

$$\phi=\phi_0+\int h(I, \theta)dv. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The very simple expressions (1) and (2) are due, I believe, to Duhem, by whom they were given in 1888. Before making use of them, I will show how the energy of a magnetized system is discussed in the ordinary text-books.

The principle of the conservation of magnetism being taken for granted, it is first assumed that magnetization may be separated from material bodies; in other words, that the property of matter of exerting actions at a distance may exist

apart from matter. It is next assumed that there is an infinite store of positive and negative magnetism at infinity at which we can be supplied gratis with as much as we require. Lastly, it is assumed that the attraction or repulsion between any two small quantities of magnetism m, m', dissevered from matter, is exactly the same as the attraction or repulsion between two small portions of matter at the same distance, magnetized with the same quantities of magnetism m, m'. Then, in order to find the energy U of any magnetized system, we suppose its magnetism made up of an infinite number of elements which were originally at an infinite distance from the given material system and from one another, and unassociated with matter. If, therefore, we denote by U_0 the energy that the given system would have if it were deprived of its magnetization, but otherwise unchanged, and imagine some agent capable of bringing the magnetic elements from infinity up to the given system, and there placing them in the positions they are to occupy, without exerting more force than is just necessary to overcome the attractions and repulsions between them, we are supposed to get

$$U = U_0 + Y.$$

The ordinary text-books make no attempt to find the entropy of a magnetized system. In fact, until the appearance of Duhem's book in 1888, the rigid methods of thermodynamics do not seem to have been thought necessary.

In order to find the condition of magnetic stability on a homogeneous body of uniform temperature θ, we suppose the body incapable of receiving or losing heat except at the constant temperature θ. Then we imagine the magnetization of a single volume element dv to change slightly in direction, and to increase from I to $I + \delta I$; and we suppose that when the temperature has again become equal to θ, no other change has been made in the system.

If δQ be the heat absorbed in the process, the principles of thermodynamics require that

$$\delta Q < \theta \delta \phi,$$

or, since no work has been done on the system during the operation,

$$\delta U < \theta \delta \phi.$$

Hence

$$\delta Y + \left(\frac{dI}{df} - \theta \frac{dh}{dI} \right) dv \, \delta I < 0,$$

or

$$\delta Y + \psi(I, \theta) dv \, \delta I < 0, \text{ (say)}. \quad . \quad . \quad . \quad (3)$$

Let us now imagine a system identical with the given system before the change in dv, and let this particular element be removed to infinity without causing any other change in the system. Then if w be the work so obtained, we have clearly

$$\delta Y = \delta w.$$

To find δw, we may take the volume dv of any form we please. Suppose it is a cylinder with its ends perpendicular to the axis, and the axis parallel to I. Then, by the principles of the potential, if $d\omega$ be the section of the cylinder and ds its length, we have

$$w = I d\omega \, ds \frac{dV}{ds},$$

or

$$w = I \frac{dV}{ds} dv,$$

where, in finding $\frac{dV}{ds}$, we travel on the line of magnetization.

Now since the potential V at any point (x, y, z) is a function only of the three coordinates of that point, we obtain, if (α, β, γ) be the angles the direction of magnetization at the point (x, y, z) makes with the axes,

$$\begin{aligned} \frac{dV}{ds} &= \frac{dV}{dx}\frac{dx}{ds} + \frac{dV}{dy}\frac{dy}{ds} + \frac{dV}{dz}\frac{dz}{ds} \\ &= \cos\alpha \frac{dV}{dx} + \cos\beta \frac{dV}{dy} + \cos\gamma \frac{dV}{dz}, \end{aligned}$$

and therefore

$$I\frac{dV}{ds} = A\frac{dV}{dx} + B\frac{dV}{dy} + C\frac{dV}{dz}.$$

Thus, since the potential at any point of the element dv, and therefore the values of $\frac{dV}{dx}$, $\frac{dV}{dy}$, $\frac{dV}{dz}$ are independent of the magnetization of that particular element when it is small enough, we obtain

$$\delta w = \left(\delta A \frac{dV}{dx} + \delta B \frac{dV}{dy} + \delta C \frac{dV}{dz}\right) dv.$$

If the element dv be to any extent magnetically "rigid," its magnetization will not be fully able to obey the directing causes, and there will be relations between δA, δB, and δC; but if the element be "perfectly soft," we may consider δA, δB, δC independent. In the latter case, if we put δB and δC both zero, equation (3) gives

$$\delta A \frac{dV}{dx} + \psi(I, \theta)\delta I < 0.$$

But since $I^2 = A^2 + B^2 + C^2$, we have, when B and C are constant,

$$I\delta I = A\,\delta A.$$

Hence, for all values of δA, we have

$$\left\{ \frac{dV}{dx} + \frac{A}{I}\psi(I, \theta) \right\} \delta A < 0.$$

If the quantity $\frac{dV}{dx} + \frac{A}{I}\psi$, within $\{ \ldots \}$, be positive, A can only decrease; if it be negative, A can only increase; if it be zero, A can neither increase nor decrease. We have, therefore, in stable equilibrium, at every point of a "perfectly soft" substance,

$$\frac{1}{A}\frac{dV}{dx} = \frac{1}{B}\frac{dV}{dy} = \frac{1}{C}\frac{dV}{dz} = -\frac{1}{I}\psi(I, \theta). \quad . \quad . \quad . \quad (4)$$

We must now explain the meaning of the differential coefficients of V. We know that if at any external point $P(x, y, z)$, a unit positive pole be placed without disturbing the magnetization of any part of the given material system, $\left(-\frac{dV}{dx}, -\frac{dV}{dy}, -\frac{dV}{dz}\right)$ will be the magnetic forces (X, Y, Z), parallel to the axes, exerted on the unit pole at P by the given system. When the point P is within the given system, we cannot place a unit pole there without disturbing the system. We therefore imagine a small right circular cylinder, whose axis coincides with the direction of magnetization and whose ends are perpendicular to the axis, removed from about the point P; and suppose that no change is made in the system beyond the removal of the contents of the cylinder. If the point P is in the midst of a liquid or gas, a thin substance, the magnetization of which may be neglected, must be used as a lining for the cylinder, so that the interior of the cylinder is vacuous. Then if V′ be the potential at P of the new system obtained by removing the contents of the cylinder from the original system, $\left(-\frac{dV'}{dx}, -\frac{dV'}{dy}, -\frac{dV'}{dz}\right)$ will be the magnetic forces parallel to the axes, exerted by the new system on a unit positive pole placed at P without disturbing the system. But if V″ was the potential at P of

the contents of the cylinder before removal, and V the potential of the whole of the given system, we should have

$$V = V' + V'',$$

and therefore

$$-\frac{dV}{dx} = -\frac{dV'}{dx} - \frac{dV''}{dx}, \text{ \&c., \&c.}$$

Now the contents of the small cylinder, before being cut away, were magnetically equivalent to layers on the ends, of densities $+I$ on the positive end and $-I$ on the negative end. Thus $-\frac{dV''}{dx}$ is simply the force, parallel to the axis of x, arising from these two layers. But if we take a circular layer of uniform density I, the force it exerts on a unit pole in the axis of the layer at a point where the radius of the layer subtends an angle α, is $2\pi I(1-\cos\alpha)$, and may therefore be neglected when α is small. Hence, if the radius of the right circular cylinder be infinitely small in comparison with the length, the differential coefficients of V'' will be zero. Consequently, $\left(-\frac{dV}{dx}, -\frac{dV}{dy}, -\frac{dV}{dz}\right)$ are the magnetic forces parallel to the axes, exerted by the new system V' on a unit pole placed at P without disturbing that system. These forces are written (X, Y, Z), and are called *the forces* of the *given* system at P.

If F be the resultant of (X, Y, Z), or the resultant force of the given system at P, equations (4) become

$$\frac{X}{A} = \frac{Y}{B} = \frac{Z}{C} = \pm\frac{F}{I} = \frac{1}{I}\psi(I, \theta).$$

Now it has been shown by Duhem (*Des Corps Diamagnétiques*) that $\psi(I, \theta)$ must always be positive. We must therefore always take the positive sign before $\frac{F}{I}$, and may write

$$\frac{A}{X} = \frac{B}{Y} = \frac{C}{Z} = \frac{I}{F} = \chi(I, \theta), \quad . \quad . \quad . \quad . \quad (5)$$

where $\chi(I, \theta)$ is always positive.

The meaning of equations (5) is that, at any point of a "perfectly soft" homogeneous substance, the magnetization, when in stable equilibrium, coincides in direction with the force at that point. If there is any magnetic "rigidity" about the substance, the magnetization at a point may, of course, make a finite angle with the force at that point.

We can now explain Weber's hypothesis of magnetism. He considers that a body which appears to be neutral is as much magnetized as when it exhibits active magnetic properties, only that, in the former case, the magnetized molecules have their axes pointing in all directions so as exactly to neutralize one another. He then supposes that the act of magnetization merely consists in giving the axes of the magnetized molecules a definite direction. In fact, if we suppose an elementary magnet suspended freely by the centre of mass, it is clear that it will set its axis in the direction of the external magnetic force which acts upon it.

In the common theory of magnetism it is admitted that in a "perfectly soft" homogeneous substance, the magnetization at any point is in the same straight line as the force; but it is supposed that in the so-called diamagnetic homogeneous "soft substances," ψ, or χ is negative, or that the magnetization is in the opposite direction to the force. This gives rise to a difficulty in Weber's theory: for it appears to follow that when an elementary magnet is freely suspended by the centre of mass, it may permanently set its axis in the opposite direction to the external magnetic force. To escape from this difficulty it might be assumed that in every diamagnetic body a number of molecules form a kind of lock-work, similar to that of a gun, and that the first act of the external magnetizing force is to set the lock. In this way, it might be thought, we should have a means of setting the magnetized molecules in the opposite direction to the force and keeping them there; but it would follow that a diamagnetic body could not be magnetized until the external magnetizing force exceeded a certain value, and would not lose its magnetization when the force was withdrawn. As this appears to be contrary to experiment, we conclude that our explanation of the difficulty due to the common theory of diamagnetism must be insufficient.

In the case of a quasi-homogeneous substance, like air or any gas, the mass-density will vary from point to point. Denoting the mass-density by ρ, and putting $\mathrm{I} = \frac{\rho}{\rho_0}\mathrm{I}'$, where ρ_0 is a standard fixed value of ρ, the state of the air or gas at any point may be defined by the three variables $(\mathrm{I}', \rho, \theta)$. If we put $\mathrm{A} = \frac{\rho}{\rho_0}\mathrm{A}'$, &c. &c., it is easy to see that equations (5), which hold for the stable distribution of magnetization, become

$$\frac{A'}{X}=\frac{B'}{Y}=\frac{C'}{Z}=\frac{I'}{F}=\chi'(I', \rho, \theta), \quad . \quad . \quad . \quad (6)$$

where χ' is always positive.

Now let the air be mapped out by equipotential surfaces and lines of force, just as in electrostatics, and imagine a small right circular cylinder described in the air with its ends at right angles to the axis and the radius of its normal section very small in comparison with the length of the axis. Then, by taking the axis of the cylinder tangential to an equipotential surface, it is easily seen that the pressure and density of the air have constant values all over the same equipotential surface. If the axis coincide with a line of force, and we suppose ourselves to travel in the direction of the force, we obtain, since the force exerted at any point by the neighbouring molecules is zero,

$$dp=I\frac{dF}{ds}ds=I'\frac{\rho}{\rho_0}\frac{dF}{ds}ds,$$

or, if we assume the simple law of gases, $p=R\rho\theta$, where R is a constant for the same gas,

$$dp=I'\frac{p}{p_0}\frac{dF}{ds}ds,$$

or

$$\frac{dp}{p}=\frac{I'}{p_0}\frac{dF}{ds}ds.$$

Integrating this equation, we get

$$\log\frac{p_2}{p_1}=\frac{1}{p_0}\int_1^2 I'\frac{dF}{ds}ds.$$

Now it is usually assumed that for the feebly magnetic substances, the positive quantity χ is practically constant, and its value is written k. We have then, in a homogeneous soft body (liquid or solid), $A=kX=-k\frac{dV}{dx}$, &c. &c., so that if ρ be the volume-density of the magnetism in the interior of the body,

$$\rho=-\left(\frac{dA}{dx}+\frac{dB}{dy}+\frac{dC}{dz}\right)=k\nabla^2V.$$

Hence, since $\nabla^2V=-4\pi\rho$, we have

$$\rho(1+4\pi k)=0,$$

and therefore $\rho=0$, or the body is magnetically equivalent to a layer of magnetism on the surface.

A similar result would follow for a gas, provided the mass-density be nearly uniform.

In air or a gas,

$$I' = kF,$$

or

$$I = k\frac{\rho}{\rho_0}F,$$

and, therefore, along a line of force in air,

$$\log\frac{p_2}{p_1} = \frac{k}{2p_0}(F_2^2 - F_1^2),$$

or

$$\frac{p_2}{p_1} = e^{\frac{k}{2p_0}(F_2^2 - F_1^2)},$$

or approximately, since k is very small,

$$\frac{p_2 - p_1}{p_1} = \frac{k}{2p_0}(F_2^2 - F_1^2),$$

that is, nearly,

$$p_2 - p_1 = \frac{k}{2}(F_2^2 - F_1^2). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In a liquid, $I = kF$, and therefore, along a line of force,

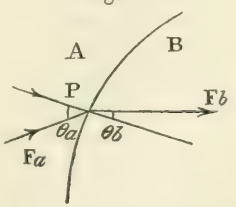
$$dp = I\frac{dF}{ds}ds = kF\frac{dF}{ds}ds,$$

and therefore

$$p_2 - p_1 = \frac{k}{2}(F_2^2 - F_1^2). \quad . \quad . \quad . \quad . \quad . \quad (7')$$

The important simplification effected by putting χ constant makes it easy to determine the abrupt change which takes place in the force when we pass from one soft body to another. For let F_a be the force just inside a soft body A and F_b the force just inside another soft body B, near any point P of their common surface; and let θ_a, θ_b be the angles F_a and F_b make with the common normal at P, drawn from A to B. Then the density at P of the surface-layer of A will be $I_a \cos\theta_a$, and of the layer of B, $-I_b \cos\theta_b$. Hence, in passing from A to B, we have

Fig. 9.



$$F_b\cos\theta_b - F_a\cos\theta_a = 4\pi\{-I_b\cos\theta_b + I_a\cos\theta_a\}.$$

If both A and B be liquid or solid, we obtain

$$(1+4\pi k_b)\mathrm{F}_b \cos\theta_b=(1+4\pi k_a)\mathrm{F}_a \cos\theta_a.$$

If A be air or any gas, and ρ be the mass density at P,

$$(1+4\pi k_b)\mathrm{F}_b \cos\theta_b=\left(1+4\pi k_a\frac{\rho}{\rho_0}\right)\mathrm{F}_a \cos\theta_a.$$

If A be a perfect "vacuum," we put $k_a=0$.

This result, which is even more important in electricity than in magnetism, can be written in a very brief form. For if F_{an}, F_{bn} be the normal components of F_a and F_b, and if μ_a stand for $1+4\pi k_a$ or $1+4\pi k_a\frac{\rho}{\rho_0}$ and μ_b for $1+4\pi k_b$, we have

$$\mu_b\mathrm{F}_{bn}=\mu_a\mathrm{F}_{an}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8).$$

The foregoing is the usual method of stating the result; but if we keep to the convention of supposing every *normal* to be drawn *outwards*, we shall have

$$\mu_a\mathrm{F}_{an}+\mu_b\mathrm{F}_{bn}=0.$$

Since for many substances k is very small (being less than $\frac{1}{4\pi\,000}$), it follows from the preceding investigation that the abrupt change of the force in crossing the boundary of two soft bodies may generally be neglected. Hence, if a number of soft, feebly magnetic bodies be magnetized by permanent steel magnets, we may suppose, without sensible error, that the force at any point is entirely due to the permanent magnets; in other words, we may neglect the force due to the magnetization induced in the soft bodies. This may also be shown as follows:—Let B be any soft, feebly magnetic body. Then the force at any point is the resultant of two forces—F_b due to B and F_a due to the rest of the system. To make a rough comparison between F_b and F_a, we take the point close to the surface of B, in which case it is evident that F_b is comparable with $2\pi\mathrm{I}_b$, that is, with $2\pi k_b\mathrm{F}$, or with the resultant of $2\pi k_b\mathrm{F}_b$ along F_b and $2\pi k_b\mathrm{F}_a$ along F_a. Thus F_b is comparable with $2\pi k_b\mathrm{F}_a$, or if $k_b=\frac{1}{400,000}$, with the 60,000th of F_a; and we draw the same conclusion as before.

Let us now suppose that a soft, feebly magnetic body B, which is either a solid or a liquid contained in a bag, is magnetized inductively by a permanent steel magnet situated

to the left; and let us imagine, for the sake of simplicity, that the magnetic force within the body B is everywhere parallel to the axis of x, so that as we travel parallel to Ox in the positive direction, the force diminishes *numerically*, whether it be the positive or the negative pole of the permanent magnet which acts on B. Then if we consider a parallelopiped on the base $dy\,dz$, the force acting on it parallel to Ox will be

$$dy\,dz\int \mathrm{I}\frac{d\mathrm{F}}{dx}\,dx,$$

or

$$k_b dy\,dz\int \mathrm{F}\frac{d\mathrm{F}}{dx}\,dx,$$

or

$$\tfrac{1}{2}k_b dy\,dz\int \frac{d\mathrm{F}^2}{dx}\,dx,$$

which is always negative, since F^2 diminishes as x increases, and k_b is positive. Hence the soft body B is always attracted by the permanent magnet. The same result would have been obtained if B had been air or a gas contained in a bag.

If the body B be immersed in air or in a gas, or in a soft liquid, the pressures on the two ends of the small parallelopiped will, by equations (7) and (7′), give a force in the opposite direction to Ox of

$$\tfrac{1}{2}k_a dy\,dz\int \frac{d\mathrm{F}^2}{dx}dx,$$

where F has the same meaning as before.

Hence if k_b be greater than k_a, or the body B more magnetic than the gaseous or liquid medium by which it is surrounded, the attraction of the permanent magnet will overpower the pressure on the surface and the body B will be drawn towards the pole of the magnet; but if k_b be less than k_a, or B less magnetic than the surrounding medium, the attraction of the permanent magnet will be overpowered by the pressure on the surface, and the body B will appear to be repelled by the permanent magnet.

We may now sum up the analogies we have found between magnetism and gravitation in the case of homogeneous bodies. First of all, every soft substance is attracted when placed near one pole of a magnet; and every body is attracted to the earth. Secondly, if a number of soft bodies be magnetized by a steel magnet, we may neglect

the action of the magnetized soft bodies on one another; and if a number of small bodies be placed near the earth, we may neglect their gravitational attraction on one another in comparison with that of the whole earth. Lastly, if a soft body be immersed in a gas or liquid, and then placed near the pole of a magnet, it will appear to be attracted or repelled according as it is more or less magnetic than the gas or liquid by which it is surrounded; and if any body be immersed in a gas or liquid, it will appear to be attracted or repelled by the earth according as it is heavier or lighter than the gas or liquid in which it is placed.

The theory we have given is beautifully illustrated and confirmed by the following experiments of Faraday's, described in Tyndall's 'Diamagnetism.' Theory and experiment fit together so exquisitely that we cannot but wonder the true theory should not have been seen from the first.

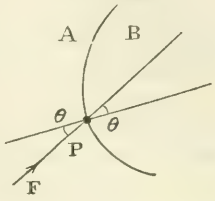
"If a weak solution of protosulphate of iron, *m*, be put into a selected thin glass tube about an inch long, and one third or one fourth of an inch in diameter, and sealed up hermetically, and be then suspended horizontally between the magnetic poles in the air, it will point axially, and behave in other respects like iron; if instead of air between the poles, a solution of the same kind as *m*, but a little stronger, *n*, be substituted, the solution in the tube will point equatorially, or as bismuth. A like solution somewhat weaker than *m*, to be called *l*, enclosed in a similar tube, will behave like bismuth in air but like iron in water."

It now remains to describe how it is generally attempted to gloss over the imaginary difficulties of diamagnetism.

It is generally admitted that the apparent magnetic or diamagnetic properties of a soft body B immersed in air or any other gas or a liquid, are merely differential—that is, depend on the algebraic excess of the coefficient k_b of the body B over the coefficient k_a of the substance A in which it is immersed. This result is thought to be "proved" in the following way:—Since every soft body is magnetically equivalent to a layer of magnetism on its surface, it follows that there are two layers on the common surface of A and B, one belonging to A, the other to B. It is then supposed that the layer on this surface which properly belongs to A, does not really belong to A at all, but to B. The body A being magnetically equivalent to a layer on its surface, it is assumed that, as the layer on the common surface of A and B is supposed transferred to B, we may treat A as unmagnetized. With this assumption the pressure of A would be uniform,

and the behaviour of B would be entirely determined by the supposed compound layer on its surface. Now if θ be the angle at any point P of the common surface of A and B between the normal at P, supposed drawn from A to B, and the force, which may be considered continuous in crossing the bounding surface, the superficial density of the layer at P which belongs to B will be $-I_b \cos\theta$, and of that which belongs to A, $I_a \cos\theta$. Hence the density at P of the compound layer is $(I_a - I_b)\cos\theta$. The ratio of this to the density at P of the layer which properly belongs to B, is $\frac{I_b - I_a}{I_b}$, which is equal to a constant $\frac{k_b - k_a}{k_b}$. Thus, since the attraction of the permanent magnet on B, due to the surface-layer which properly belongs to B, may be written $k_b G$, where G would have the same value for any soft body of the same shape and size as B, when placed in the same position, the attraction of the permanent magnet on B, when immersed in A, will be $(k_b - k_a)$ G, or equal to the force due to the layer which properly belongs to B, diminished by what this force would be for the gas or liquid, A, displaced by B.

Fig. 10.



According to the remarkable caricature of reasoning just noticed, it follows that we do not need to know the absolute value of the coefficient k belonging to any soft substance, but merely the algebraic excess of the coefficient over that of some standard substance. This standard "substance" is often chosen to be a "vacuum," and its coefficient is put zero. Then, since many bodies are apparently repelled by a magnet pole in a comparatively slight "vacuum" of 2 to 3 millimetres of mercury, it is concluded that the coefficients of these bodies, or, rather, the excesses of their coefficients over that of a vacuum, are negative.

Granting, for the present, the first part of this so-called reasoning, we must point out that a vacuum can only be obtained by removing the air completely from the interior of a closed vessel, and not by merely reducing the pressure to 2 or 3 millimetres of mercury. If we were allowed to consider such a comparatively slight reduction of density as constituting a vacuum, we could prove the existence of diagravitation; for if we could find a gas 100 times as light as hydrogen, a balloon could be made which would float in this so-called vacuum.

We must now consider the two layers on the common surface of two soft bodies A, B, A being a gas or liquid. If the surface-molecules of A were provided with sharp points and were caused by the smallest amount of magnetization to stick to B, it might be thought that both surface-layers would then belong to B; but a little consideration tells us that the molecules which stick to B would take with them two layers of opposite signs, and it is clear that the remainder of A would still have a surface-layer of its own, adjoining the modified surface of B. In order, therefore, to cause the two surface-layers both to belong to B, we must make the following assumptions:—It must be supposed that every molecule of A is provided with a sharp point, and that the act of magnetization causes each molecule to be broken into two halves, on one of which is the positive magnetism, on the other the negative. Then it must be supposed that those half-molecules on which are the surface-layers of A stick to the bodies B . . . , with which they happen to be in contact, and lastly, that the other half-molecules stick together in pairs in such a way that their magnetisms neutralize one another. In this way, we should have both surface-layers belonging to B, and we might treat the free part of the gas or liquid A as unmagnetized. A difficulty would, however, arise when the magnetizing force was withdrawn, unless we had some means of reminding the half-molecules to take partners. We might avoid the difficulty by imagining the two halves of each molecule tied together by a piece of thread, but then we should introduce the absurdity that magnetization changed the gas or liquid A into a solid. Lastly, we should be obliged to conclude that when a system is once magnetized, it is impossible to increase the magnetization—a conclusion which, of course, is necessarily false.

There is one other way of treating diamagnetism which requires to be noticed. This is the method of induced electric currents used by Weber, by which it is thought to be proved that k is negative for bismuth and some other substances. To this I reply that I have already sufficiently disproved the common theory of diamagnetism; and secondly, it will be proved in a future paper that the common theory of induced currents generally involves an absurdity, and can seldom be correct.

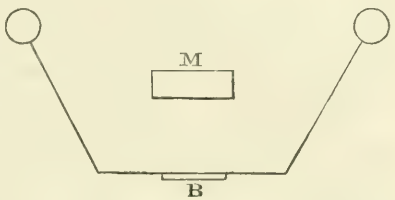
The rest of the paper will be occupied with a brief discussion of a few important problems in the light of the new theory.

I. If a body P, placed near a number of fixed bodies X, Y, Z, ... , be subject to no actions at a distance, but those of

magnetism and gravitation arising from the fixed bodies X, Y, Z . . . . , it can easily be shown that no state of equilibrium of the body P can be stable unless it be in material contact with one or more of the fixed bodies. This proposition is proved in Duhem's *L'aimantation per influence*. When P is in material contact with one or more of the fixed bodies, its equilibrium may, of course, be stable. The most useful case to consider is the following :—

Imagine a small bar of bismuth B, suspended from two small balloons by threads, as in the figure, and suppose that the mass of the system is slightly less than the mass of the air which it displaces when unmagnetized and near the ground. Then, if the system be set free, it will ascend in the air, and, of course, a state of stable equilibrium will be attained when it has risen high enough, if the weather be calm. We may, however, obtain a state of stable equilibrium in a more convenient way. For if a permanent strong steel magnet M be fixed some distance from the ground, just over the bar B, the system of the bismuth and balloons, when let go, will ascend until the motion is checked by the increased density and pressure of the air about M, and will ultimately take up a state of stable equilibrium suspended in the air at a moderate distance from the ground.

Fig. 11.



The problem just given was, we believe, first considered by Sir W. Thomson, to whom it was suggested by the story of the coffin of Mahomet.

II. We will next consider the thermal phenomena due to the motion of a soft body B in presence of a permanent magnet M. For simplicity, let M be held at rest and suppose its magnetism "rigid." Also let B be homogeneous, and let our magnetized system consist merely of the two bodies B and M, situated in a vacuum. Then if the temperature, in every state of equilibrium, is uniform and equal to θ, and if no heat can be absorbed or given out except at the temperature θ, we shall have, in any small reversible operation,

$$\delta Q = \theta \delta \phi.$$

Now the formula for the entropy is

$$\phi = \phi_0 + \int h(\mathrm{I}, \theta) dv. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We have, therefore, if no appreciable change takes place in the form or size of B,

$$\delta Q = \theta \int \frac{dh}{dI} \delta I \, dv,$$

where the integral refers only to the soft body B, since no change can take place in M.

If the operation consist in moving B nearer to M, I will increase or δI be positive. Hence, if $\frac{dh}{dI}$ be positive for all values of I, the operation will cause an absorption of heat, or would cool the body B, if heat was not supplied from without: if $\frac{dh}{dI}$ be always negative, there will be an evolution of heat, or the operation would heat the body B.

III. We will, last of all, examine, with Duhem, the method proposed by Jamin for the determination of the distribution of magnetism on a permanent magnet.

A small piece of soft iron, B, being placed in contact with the permanent magnet at any point P, the smallest force required to detach it is measured, and it is supposed by Jamin that this force is proportional to $\left(\frac{dV}{dn}\right)^2$, where V is the potential of the permanent magnet at P and dn an element of the outward drawn normal.

We observe, in the first place, that the small piece of soft iron B is magnetically equivalent to a layer on its surface. Consequently, the magnetic force at any point is the resultant of that due to the surface-layer of B and of that due to the permanent magnet. Within the body B, the force due to the surface-layer of B is the greater of the two. This will complicate the problem, and so, for the sake of argument, we will agree to ignore the surface-layer of B. With this assumption, it follows that the equipotential surfaces and lines of force will be due entirely to the permanent magnet, and that the *total* magnetic force exerted on B by the permanent magnet acts along the line of force at P, and is equal to $I\frac{dF}{ds} dv$, where dv is the volume of B, and ds an element of the line of force *in the positive direction of* F. If, for simplicity, we put $I = kF$, this result becomes $\frac{1}{2}k\frac{dF^2}{ds} dv$. Now if the line of force at P be directed outwards, $\frac{dF^2}{ds}$ will be negative, and if it be directed inwards, $\frac{dF^2}{ds}$ will be positive. Thus in both

cases, the total magnetic force exerted by the permanent magnet on B is an attraction; and its component along the outward-drawn normal is $\frac{1}{2}k\frac{dF^2}{dn}\,dv$.

Thus even with all our assumptions, the force which Jamin requires to be measured is proportional, not to $\left(\frac{dV}{dn}\right)^2$, that is to F^2, but to $\frac{dF^2}{dn}$.

The preceding three examples, and many others, are discussed in Duhem's *L'aimantation par influence*—a book which seems to contain the first systematic application of the principles of thermodynamics to magnetism.

XXXV. *The Expansion of Chlorine by Light as applied to the Measurement of the Intensity of Rays of High Refrangibility.* *By* Dr. A. Richardson, *Lecturer on Chemistry, University College, Bristol**.

[Plates III. & IV.]

It has been shown by Budde (Phil. Mag. iv. 1871; Pogg. *Ann.* Ergbd. vi. 1873) that when chlorine is exposed to the influence of sunlight, an expansion of the gas occurs which is independent of the direct heating-effects due to the light; the volume to which the gas first expands is maintained during exposure provided that the intensity of the light remains constant, contraction to the original volume taking place when the gas is shaded. He further found that the rays of high refrangibility were influential in promoting this change, no expansion being occasioned by the rays at the red end of the spectrum. The application of this property of chlorine to the measurement of the "actinic"† intensity of light was suggested by Budde many years ago, but no further steps appear to have been taken in this direction.

Some experiments on which I am at present engaged have rendered it necessary that the actinic intensity of light should be measured during periods of many months together, and it seemed possible that the expansion of chlorine by light might be applied to this purpose. As, however, the researches of Bunsen and Roscoe (Trans. Roy. Soc. 1887, p. 381) led them to the conclusion that no change in volume occurred in chlorine, when exposed to light, other than that due to direct heating-effects, it became necessary to repeat some of Budde's experiments so as if possible to decide this point. In order to do this

* Communicated by the Physical Society: read June 26, 1891.

† The term "actinic" is used for brevity to denote rays at the violet end of the spectrum.

a differential apparatus was taken, consisting of two bulbs of 160 cubic centim. capacity each and connected by a capillary tube containing strong sulphuric acid ; any change in pressure of the gas in either bulb was indicated by the movement of an index of air contained in the capillary.

The bulbs were first filled with dry air and placed in a glass tank through which a current of cold water circulated ; under these conditions it was found that no movement of the index took place on exposure to bright sunlight. The air in one of the bulbs was then replaced by dry chlorine, and both bulbs were again exposed under precisely similar conditions ; an immediate expansion of the chlorine took place, causing the index to move through a distance of from 20 to 30 centim., but on shading the bulbs the index returned to zero. On interposing variously coloured glasses between the bulbs and the source of light, it was found that with cobalt glass the index receded 15 to 20 centim. from the zero-point, whilst even faintly yellow glass as well as ruby glass caused it to return to zero. It was further found that the radiations from a cannon-ball at a temperature just below a red heat produced practically no movement of the index when the bulbs were exposed in the air at a distance of from 1 to ·5 metre.

Budde's observations being thus confirmed, it was next necessary to determine how far the expansion of chlorine is proportional to the actinic intensity of the light to which it is exposed. In order to do this a series of measurements of the expansion of the gas were made, whilst at the same time the intensity of the light to which the gas was exposed was determined by means of an actinometer.

The expansion of the gas was measured in a differential arrangement, consisting of two tubes of 55 cubic centim. capacity and 10 centim. in length ; these were connected with a horizontal gauge graduated in ·5 centim., provided with a small bulb at each end. These bulbs and also the gauge contained strong sulphuric acid, a short column of air being introduced to serve as index.

The tubes to be exposed were suspended in a box, which could be placed at any required angle so as to face the sun, and when filled with dry air were found to be equally heated; the bulbs containing the acid were in all cases protected from the light. One tube was then filled with dry chlorine and the acid up to the index was saturated with the gas.

The chlorine used in this and subsequent experiments was prepared by the action of hydrochloric acid on potassium bichromate ; traces of hydrochloric acid were removed by passing the gas through U-tubes containing solutions of chromic acid,

and subsequently dried by means of sulphuric acid. In order to determine the actinic intensity of the light, a modified form of Bunsen and Roscoe's pendulum-actinometer was used (Trans. Roy. Soc. 1862, p. 139); in this method paper coated with silver chloride is exposed to light, and the time required to produce a degree of darkening equal to a standard tint is measured. The intensity of light necessary to produce this tint in one second of time is taken as the unit of intensity. The measurements were made in the open air, care being taken that the air- and chlorine-tubes were exposed to light in the same plane as the sensitive paper. When the maximum expansion of the chlorine was reached at any one time, as shown by the index remaining stationary, the intensity of the light was measured by exposing the sensitive paper. Two series of observations were made under widely different conditions of light; one on June 8, which was a cloudy day, the other on June 9, on which the sun was shining. The results of these measurements are given in the following table:—

Time.	I. Intensity of light (unit = 1).	II. Expansion of Cl, expressed in centimetres on scale.	III. Ratio $\frac{I}{II}$.	IV. Recalculation of intensities from observed expansion.
First Series.				
m. s.				
2 50	0·0242	1·95	0·0124	0·0263
2 55	0·0571	3·20	0·0178	0·0432
3 0	0·0461	3·20	0·0144	0·0432
3 5	0·0291	1·87	0·0155	0·0252
3 15	0·0196	1·40	0·0140	0·0188
4 0	0·0382	2·70	0·0141	0·0364
Second Series.				
10 45	0·3758	28·15	0·0133	0·3799
10 50	0·1022	7·95	0·0128	0·1073
11 0	0·1693	12·2	0·0138	0·1647
11 5	0·3240	27·95	0·0116	0·3773
11 15	0·4381	26·20 ?	0·0167	0·3537
11 30	0·3348	28·0	0·0119	0·3779
11 35	0·3212	29·95	0·0107	0·4042
11 36	0·4457	30·80	0·0144	0·4158
12 20	0·0779	6·15	0·0126	0·0890
12 30	0·1210	7·70	0·0157	0·1040
12 32	0·1087	7·65	0·0142	0·1032
12 35	0·1133	9·25	0·0122	0·1249
4 0	0·1108	10·75	0·0103	0·1451
4 5	0·1141	10·05	0·0113	0·1357
4 15	0·1150	7·75	0·0148	0·1046

In column I. the intensity of the light is given as measured by the actinometer. In column II. the expansion of the chlorine, as shown by the movement of the index from zero, is given in centimetres; the zero-point, which was determined from time to time by shading the tubes, was found to remain nearly stationary throughout. The calculated intensity, in terms of the movement of the index through 1 centim., is given in column III., and from the mean value so obtained the intensity is recalculated in terms of the observed expansion (column IV.). In making these observations great difficulty was experienced owing to the constant variation in the intensity of the light; and as the maximum movement of the index was only reached after some time, these sudden variations, which were registered accurately by the actinometer, did not produce a corresponding change in the position of the index. The close agreement between the results obtained directly by the actinometer and those calculated from the expansion of the gas lead, however, to the conclusion that the change in volume in chlorine gas is directly proportional to the actinic intensity of the light to which it is exposed, although the friction of the acid in the gauge tends to smooth out the more sudden variations.

By the aid of such a differential apparatus as that above described, to which the name of "chlorine actinometer" may be applied, the intensity of the light can be read directly from the gauge, and it is thus found possible to study other light-effects under constant conditions of intensity by making exposures whenever the index stands at a given point.

It was next necessary to inquire how far dilution with air influenced the amount of expansion of chlorine when exposed to light. To do this a differential apparatus, shown in fig. 1, Plate III., was used, in which the gas to be exposed was contained in the tubes A and B, 15 centim. in length and about 3 centim. in diameter. Two glass stop-cocks, C and D, were sealed on to A, the lower one, D, being connected with a graduated pipette E containing air and dipping under strong sulphuric acid contained in F. The graduated capillary tube G was filled with strong sulphuric acid, as also the bulbs H and I, the movement of a short column of air serving to indicate any change in volume in either tube. The tube A was first filled with chlorine, whilst B contained dry air throughout the experiment. Both tubes were then exposed to light and the expansion of the chlorine determined, the intensity of the light being at the same time noted by means of the chlorine actinometer; the tubes were then shaded and the zero-point found. The stop-cocks C and D were then

opened, and by blowing air in at the side tube J a measured volume of acid was caused to rise in E, thus forcing an equal volume of air into A. Chlorine being expelled at C; C and D were then closed, and, after the gas had thoroughly mixed, the tubes were again exposed to light of the same intensity as in the first case: this process was repeated until all the chlorine was replaced by air. Knowing the capacity of A and the proportion of air introduced at each operation, the amount of chlorine could be calculated. Two series of experiments were made under different conditions of light, the intensity for each series remaining nearly constant. The results are given in the next table.

First Series.

No.	Expansion of Cl in centim.	Per cent. of Cl in gas.	Expansion of Cl in actinometer.	Corresponding intensity of light (unit = 1).
1.	26·5	100	8·0	·1107
2.	14·5	63·7	7·9	·1092
3.	9·25	41·0	17·9	·1092
4.	5·25	26·1	17·9	·1092
5.	4·75	7·1	7·9	·1092
6.	2·0	2·0	7·9	·1092
7.	0·5	0·5	7·95	·1100
8.	0·0	0·1	7·9	·1092

Second Series.

No.	Expansion of Cl in centim.	Per cent. of Cl in gas.	Expansion of Cl in actinometer.	Corresponding intensity of light (unit = 1).
1.	11·7	100	3·55	·0491
2.	6·25	63·7	3·5	·0484
3.	5·95	41·0	3·5	·0484
4.	4·35	11·3	3·3	·0456
5.	1·0	3·0	2·2	·0304
6.	0·15	0·8	3·4	·0466

It is seen from the double nature of the curve, fig. 5, Plate III., that the first effect of dilution is very marked, diminishing after a time, and finally increasing when only a small per cent. of chlorine remains in the tube. It was found, however, that chlorine was gradually given off (from the sulphuric acid which was saturated with the gas) to such an extent that, after complete expulsion of the chlorine by air,

on again exposing the tube to light, after two days, an expansion of 5 centim. occurred. This is a point of some importance where the expansion of chlorine as against air is made a measure of the actinic intensity of light, as the diffusion of chlorine from the sulphuric acid into the air-bulb would introduce a gradually increasing source of error*.

As it seemed possible that the sensitiveness of chlorine to light might be influenced by the temperature of the gas during exposure, an experiment was made in which the two tubes A and B, fig. 2, Plate III., were filled with chlorine, these were connected together by a tube which could be closed by means of a stop-cock F ; changes in volume being measured as before by means of the gauge C containing sulphuric acid and bubbles of air. The tube A was kept at a temperature of 14° C. by a current of water circulating through the outer tube D, whilst B was heated in the jacketing tube G G, by the vapour from chlorobenzene boiling in E at a temperature of 132° C. The pressure in the two tubes was at first equalized by opening the stop-cock F ; and when the temperature was constant in the two tubes (as shown by the index remaining stationary when F was closed), the tubes were alternately exposed to and shaded from the light. The following is the mean of a series of experiments made :—

Both tubes shaded, zero	=	0.
Heated tubes exposed	=	6·0 centim. expansion.
Both tubes shaded, zero	=	0.
Cooled tubes exposed	=	6·7 centim. expansion.
Both tubes shaded, zero	=	0.

In the heated tube the illumination of the gas was interfered with by the partial refraction of the light, due to the condensation of the chlorobenzene on the sides of the jacketing tube, and further it is possible that the vapour of chlorobenzene may absorb a portion of the actinic rays. This probably accounted for the slight difference observed in the expansion of the gas in the two tubes. From this experiment it is concluded that the expansion of chlorine by light is practically unaffected within a range of temperature between 14° and 138° C.

Having made these preliminary experiments, an apparatus was next devised whereby the automatic registration of the actinic intensity of light was effected by the expansion of chlorine. This was done by suspending a differential appa-

* In the chlorine actinometer it is found desirable to cut off communication between the two bulbs, when not in use, by means of a stop-cock.

ratus on the beam of a balance in such a manner that the flow of acid from one arm to the other produced a movement of the beam, which was communicated by means of a lever to a pen and was recorded on a rotating drum.

As has already been stated, a differential actinometer, containing air in one bulb and chlorine in the other, gradually becomes inaccurate owing to the diffusion of chlorine into the air-bulb. This difficulty is avoided in the apparatus shown in fig. 3, Plate III., which consists of two differential arrangements A B C D and E F G H, suspended on the beam of the balance I; one is completely filled with dry chlorine, the tubes B and D being half filled with strong sulphuric acid saturated with the gas. The second contains dry air with sulphuric acid in F and H. One of the chlorine-bulbs A and one of the air-bulbs E are exposed to light, whilst the other chlorine-bulb C and air-bulb G are protected from the light by a covering of tin-foil, and hang in the box J, in which the two bulbs can swing freely. It will be seen that when A and E are exposed to the heating-effects of sunlight, the expansion of the gas in A causes acid to flow from B to D, whilst a corresponding expansion in E causes an equal weight of acid to flow from H to F. But the chlorine in A undergoes a further expansion, due to the actinic rays, causing an additional weight of acid to pass from B to D. A movement of the beam is thus produced which is communicated to the lever M, and is registered by means of a pen on a strip of curve-paper rotating on the drum N. The capacity of the bulbs A and E in this case is 273 cub. centim., that of G and C 319 cub. centim.; the tubes B and F and D and H are 15 centim. long and 1·25 centim. in diameter, the distance between the two sets of tubes being 35 centim. It is found desirable that the movement of the bulbs and beam should be as small as possible, and that the effect should be magnified by increasing the length of the lever. After the apparatus is blown together, care must be taken to remove all moisture by drawing dry air through the bulbs and tubes. The apparatus is exposed out of doors in a wooden box G, fig. 4, Plate III., the bulbs A and B passing through a hole in the lid; these are protected by a glass shade, C, 45 centim. high and 20 centim. in diameter; this is mounted in a block of wood, D, so that when the box is in its normal position, the axis of the cylindrical shade points to the pole star. The two bulbs occupy a position equidistant from the sides of the shade and about midway between the top and bottom. The tube E serves as a ventilator and should be at least 2·5 centim. in diameter; the cap F protects the opening from

rain, &c. The bulbs were tested, when filled with dry air, by exposing them to intense sunlight : it was found that, although the temperature within the shade varied from 15° to 40° C., the compensation was so complete that practically no deviation from the straight line, described by the pen on the drum, was observed ; the bulbs were fixed to the beam (as nearly as possible over the point of support) by means of cylinders of thin sheet-brass, which were slipped over the acid tubes and screwed to the beam. The instrument was calibrated by means of the silver-chloride actinometer. The result of six series of observations gave the following values in intensity units corresponding to one division on the curve-paper :—

1	series	mean of	11	observations	·021
2	,,	,,	14	,,	·029
3	,,	,,	10	,,	·043
4	,,	,,	15	,,	·025
5	,,	,,	9	,,	·033
6	,,	,,	10	,,	·029

Mean = ·030

In the following table the observation from one of the series is given :—

Intensity (unit = 1).	Value of 1 division in light units.	Recalculated intensity from curve.	Time of day in hours.
0·3758	0·0385	0·2925	10·75
0·1022	0·0328	0·1275	10·8
0·1693	0·027	0·1875	11·0
0·3240	0·035	0·2475	11·08
0·3348	0·029	0·3375	11·5
0·3210	0·030	0·3150	11·6
0·4457	0·039	0·3375	11·65
0·0779	0·017	0·1350	12·3
0·1087	0·021	0·1500	12·6

The curve from which the data are obtained is shown in fig. 1, Plate IV., the value of one division being equal to $\frac{1}{10}$ of a square therein represented.

In fig. 2, Plate IV., the results obtained above are multiplied by 100 and represented graphically. Fig. 3 represents the curves registered by the recording apparatus under varying conditions of light from June 13 to 16. It will be seen that such an instrument as this will record continuously the actinic intensity of the light under all conditions of weather throughout the year, and requires no attention further than winding the clock whereby the motion of the drum is maintained.

XXXVI. *On the Electrification of Steel Needle-Points in Air.* *By* A. P. Chattock *.

[Plate V.]

§ 1. As Faraday long ago put it, the discharge of electricity from a point into a gas may be looked upon as a particular case of sparking between a conductor (the point) and a non-conductor (the surrounding gas). It is, moreover, a particularly interesting form of discharge, as compared with that taking place between two conductors, from the fact that it seems more likely to throw light on the unsymmetrical behaviour of positive and negative electricity. For there is evidence which points to the surface of the electrode as the origin of that want of symmetry; and by experimenting with one electrode only, one is able to a certain extent to separate its effect on positive electricity from that on negative: such separation being impossible in the case of sparks between two conductors, as both effects are there necessarily present together.

The phenomena connected with discharge from points group themselves naturally under two heads:—Those occurring before or at the beginning of discharge; and those occurring during the passage of electricity from the point. What follows refers to the first of these divisions only.

§ 2. When an earth-connected sewing-needle is placed with its end facing the centre of an insulated metal plate, and the latter is gradually electrified, there comes a point at which the needle begins to discharge onto the plate. This point, for given conditions, is very definite, and corresponds to a breaking down of some resistance between the needle and the plate. It seemed desirable to discover how much of the dielectric was concerned in this process. For this purpose measurements were made of the strength of the electrostatic field at the surface of the needle-point at the instant that discharge occurred, the distance of the plate from the needle being varied from 0·04 centim. to 5 centim., while the needle was suspended in such a manner (§ 8) that the attraction between it and the plate could be determined.

Now the attraction is due of course to the tension in the lines of force which end at the surface of the needle; and since their direction is everywhere normal to the surface, it follows that if the needle be a true cylinder placed symmetrically with regard to the plate, the mechanical pulls of

* Communicated by the Author.

the lines of force upon its sides will balance, and the needle will be urged towards the plate with a force which depends only on the lines ending at its point (its other end being shielded from induction). Moreover, so long as the distance from the point to the plate is greater than a few times the diameter of the point, the distribution of electricity on the latter will be practically independent of that distance ; and the strength of the electrostatic field just in front of the point will thus come to be proportional to the square root of the mechanical pull on the point. The needle becomes in fact its own electrometer, and measures the difference of potential between its point and the air a short distance from it.

In Table I. the values of the square root of the pull (P) in dynes on the point of a fine* sewing-needle at the instant of discharge are given for various distances (d) in centimetres between its point and a metal plate. The constancy of $\sqrt{P}$ speaks for itself.

It is true that an ordinary sewing-needle is not a perfect cylinder, but tapers gradually to its point, so that part of P must be due to lines of force on its sides ; but this must be very small, for the density of charge on the sides is small compared with that at the point, and the force per square centimetre is proportional to the square of the density ; and in addition to this, the force on the sides has to be resolved into a direction almost at right angles to itself before it can affect P. Indeed, the very constancy of P, when d is varied, may be regarded as evidence that this part of P is negligible. (Other reasons are given in § 3.)

The two needles A and B on which the measurements were made were numbered alike by the makers, and the agreement in the values of $\sqrt{P}$ for the two is fairly close. This is the more satisfactory as the readings were taken under somewhat different conditions. The needle A was suspended in the larger of the two instruments described in § 8. It discharged onto a disk of tin 13 centim. in diameter, with its edge protected by a ring of thick wire. The disk and the inside of the instrument were covered with a thin film of vaseline. The readings on B were taken with the small instrument. The disk in this case was a penny with its surface ground and polished. No vaseline was used.

The positive values of $\sqrt{P}$ for the two needles differ by about 3 per cent., whereas the negative values differ by 10 per cent. This is worth pointing out, as it is in accordance with what appears to be a general rule, viz., that the positive

* Sharp's Egg-eyed needles, No. 10.

TABLE I.

Needle A.			Needle B.			
	$\sqrt{P}$.			$\sqrt{P}$.		
	+	−		+	−	
d.	Discharge.	Discharge.	*d.*	Discharge.	Discharge.	V.
1·35		1·31	1·27		1·18	20·6
		1·33			1·19	20·7
		1·29		1·58		28·6
		1·31		1·60		28·0
		1·28			1·15	20·4
		1·27			1·17	20·4
		1 26		1·60		28·1
		1·27		1·59		28·0
	1·62		1·08		1·18	17·4
	1·65				1·18	18·0
	1·63			1·61		23·2
		1·26		1·62		23·5
		1·27	0·76		1·17	12·4
		1·26			1·14	12·6
		1·26		1·60		17·3
	1·64			1·59		17·3
	1·64		0·45	1·61		12·3
	1·63			1·60		11·8
	1·64				1·15	8·47
		1·28			1·18	8·89
		1·28	0·28		1·16	7·10
		1·27			1·12	6·73
		1·29		1·53		9·08
3·0		1·27		1·57		9·51
		1·27	0·15	1·59		7·18
		1·28		1·59		7·18
	1·64				1·13	5·36
	1·65				1·15	5·41
	1·65		0·10		1·13	4·63
5·0	1·64				1·17	4·63
	1·66			1·56		6·05
	1·66			1·59		6·27
		1·27	0·04	1·58		5·14
		1·28				
		1·30				
		1·29				
	1·64	1·28		1·59	1·16	

discharge is more constant and stable than the negative, and far less dependent on the condition of the discharging point.

§ 3. One may, however, go further than simply showing the constancy of the discharge field at the point. In terms of the attraction of the needle and the radius of curvature of the point, it is possible to calculate its value.

Let da represent an element of area of the point's surface, and θ the angle between the direction of the lines of force at da and the axis of the needle. Then if the pull on the needle towards the plate be P,

$$P = \frac{1}{8\pi}\int f^2 \cos\theta \, da$$

over the surface of the point, f being the field-strength at da.

Take now the case of a needle with its point ground to a hemisphere; and assume (what will not be strictly true) that the value of f is uniform all over it (see below). Then the above equation becomes

$$P = \frac{r^2 f^2}{8} \text{ or } f = \frac{\sqrt{8P}}{r},$$

where r is the radius of curvature of the point. The average value of $\sqrt{P}$ for positive discharge from needle B (Table I.) is 1·59. That for negative is 1·16. The value of r for so fine a needle is rather uncertain, as it tapers towards the point. Measured under a microscope it seems to lie between $1{\cdot}9 \times 10^{-3}$ and $2{\cdot}3 \times 10^{-3}$ centim. Taking the mean of these numbers, one obtains the value of the field of force f close in front of the point

$$f = \frac{\sqrt{8P}}{r} = 2140 \text{ E.S. units for + discharge.}$$

$$= 1560 \quad \text{,,} \quad \text{,,} \quad - \quad \text{,,}$$

The highest measured value of f for discharge in air is, I believe, that obtained by Dr. Liebig for sparks between plates (Phil. Mag. July 1887, p. 106), viz. 400 E.S. units for a spark-length of 0·0066 centim. This is much less than either of the above numbers, but the length of discharge at the point is probably much less than 0·0066 centim. The results may, moreover, be verified by calculation from potential data.

Although the value of f is so large at the surface of the needle-point, the lines of force diverge rapidly, and at a very short distance from the point the field becomes inappreciable. In other words, there occurs within this short distance a step of potential (v) which, if the point is hemispherical and small, may be taken as equal to $\frac{Q}{r}$, where Q is twice the charge on the hemisphere (Q, as already assumed, being uniformly distributed over the point).

In the same way, $f = \frac{Q}{r^2}$, whence

$$v = \frac{Q}{r} = fr = \sqrt{8P},$$

the value of v being thus independent of the somewhat uncertain quantity r.

For needle B,

$v = 4{\cdot}5$ E.S. units for + discharge

$= 3{\cdot}3$ „ „ − „

In order to verify the above values of f it will be convenient and sufficient to show that these values of v calculated from P are in agreement with those calculated from potential measurements.

The column headed V in Table I. gives the difference of potential in E.S. units between the needle and the plate. Now, except for the presence of the needle itself, the field of force in which it was placed would have consisted of parallel lines; for the point of the needle was arranged in this experiment to project 3 or 4 millim. beyond a flat screen of tin-foil through a small hole in it, and the distance from the tin-foil to the disk (a penny) onto which the needle discharged was small compared with the diameter of the disk, so long as the value of d was less, say, than a centimetre. Even with the needle in position, the field would be disturbed for a very small distance only round about the point, on account of the extreme smallness of the latter. Hence V may be regarded as consisting of two parts—one constant (viz. v) and occurring in a small space close to the point; the other proportional to d for small values of d.

Taking the mean of the values of V for each value of d, we obtain the numbers plotted with d in Curves I. The upper curve is for positive discharge, the lower for negative. Up to a distance of something less than a centimetre from point to plate, the values of V lie very fairly on the straight lines ruled through them. V − a constant is thus proportional to d; and the values of the constants are of course to be found where the ruled lines cut the axis of V. These points are hardly distinguishable from the values (which are marked by crosses) of the step of potential at the point calculated above from P (viz. 4·5 and 3·3). They show indeed a slight tendency to exceed these values; but the agreement is certainly striking, considering the complete independence of the two methods of measurement.

The small amount (3 to 6 per cent.) by which the potential step calculated from V exceeds that calculated from P may be accounted for, I think, by the fact that the lines of force from the needle-point do not diverge quite as rapidly as calculation supposed. The parallel lines of the rest of the field keep them together and so increase the real step of potential at the point without altering P in proportion. To test this point I measured P for a needle of about the same size as B, first suspending it in a parallel field, and then with its point at the centre of curvature of a spherical cup. In the first case, $\sqrt{P}$ was about 3 or 4 per cent. less than in the second; showing, as it seems to me in the light of what follows, that, in the parallel field, f at the point was nearer the average value of the field through a small distance from the point surface than in the radial field of the second case; and to about the same amount that the above discrepancy requires.

This accounts, moreover, for the fact that needle B is the only one which does not agree with the results of Table II. Its constant ($f \times r^{0\cdot8}$) being 15·5 at a pressure of 76 centim.

As regards the measurement of potential in the above, the electrometer described in § 8 was used; its constant being determined by comparison with short sparks between brass knobs of 5·3 centim. diameter.

The following are the readings taken :—

Spark-length.		V from spark-length (E.S. units).	$\sqrt{\text{Electrometer-reading.}}$	Constant of electrometer.
Observed.	Corrected for flat plates.			
0·127	0·125	17·8	6·63	2·69
,,	,,	,,	6·63	2·69
0·190	0·186	24·8	9·23	2·68
,,	,,	,,	9·30	2·67

The values of V were taken from Dr. Liebig's paper already referred to.

I think, then, it may be safely concluded that the attraction of a plate on a needle-point is practically due *only* to the lines of force ending at its point—even when the needle is not a perfect cylinder; for a conical point could only have the effect of increasing P and so making the step of potential calculated

from it bigger than that from V, whereas the reverse is the case. It is true that the density must be greater at the centre of the point than at the sides of the hemisphere. But this is what P chiefly depends upon, and it is also precisely here that discharge occurs and the value of f is required. Hence the connexion established above between P and f seems to be practically true, although the assumption that f is uniform over the point-surface is not.

In what follows, therefore, the values of f have in every case been determined from P and r.

Effect of Curvature of Discharging Surface.

§ 4. Two conclusions appear, then, to result from the foregoing. In the first place, the absence of discharge below a certain definite potential, which is constant for given conditions, implies the breaking down of some resistance before electricity can pass off at a point ; and, secondly, the fact that f is independent of d points to the near neighbourhood or actual surface of the point as the seat of this resistance.

All this is in accordance with what is known regarding the discharge of electricity in gases, and is indeed only what one would naturally have expected. It still remains to consider whether the resistance to discharge is to be sought in the gas itself, in the surface of the point, or in both.

The possible ways in which resistance may arise are, I think, all to be included under three heads :—

(*a*) It may exist in the gas itself, to a greater than molecular distance from the point. For this the gas must become possessed of something in the nature of structure round about the point (*i. e.* cease to be gas in the ordinary sense of the word), and the only kind of structure that suggests itself as likely is that of the polarized Grotthuss chains which Prof. J. J. Thomson has used with such effect in his beautiful theory of striæ.

(*b*) It may exist at the surface of the metal only, and consist in the tearing away from the point by electrical force of electrified particles which are clinging to it (a special case of which is the forcing of charged particles through a non-conducting layer on the point).

(*c*) Or it may mean the pulling off of something in the nature of a film possessing surface-tension.

As a matter of fact (*b*) and (*c*) are two opposite extremes of the same phenomenon. In both, particles adhering to the point are pulled off—but the adhesion of (*b*) is normal to the surface only, *i. e.* between the particles and the metal ;

while in (*c*) it is tangential to the surface only; *i.e.* between the particles themselves. An actual case would lie somewhere between the two; and probably much nearer to (*b*) than to (*c*).

Now in the case (*a*) of Grotthuss chains the field f at the point, as measured by the pull upon it, should increase as the sharpness of the point increases; and for two reasons. In the first place, for chains of given length there will be some average strength of field required to break them, the value of which will always be less than that measured at the surface of the point on account of the divergence of the lines of force there; and the difference between the measured and the average field will be more marked as the divergence (*i.e.* the sharpness of the point) increases. Secondly, the chains will be shorter at a sharp point than at a blunt one on account of this same divergence; and this again will necessitate a stronger field to break them, for much the same reason that a short piece of iron is harder to magnetize than a long one.

The same sort of variation of f with sharpness of point will occur in the case of (*c*), if the mechanical pull of the field on the point surface be looked on as having to tear off a film stretched over it.

But to pull small particles off a point whose radius of curvature is large compared with their diameters will always require the same value of f. Hence (*b*) differs from (*a*) and (*c*) in requiring that f shall be independent of r.

The effect on f of altering r was therefore investigated. Steel needles were ground by a watchmaker to hemispherical points of different diameters and burnished with a hard steel tool. The values of f in air were then determined for each at various pressures; the instrument used being the smaller of the two described in § 8. Curves connecting air-pressure (p) and f were then plotted, and from these the numbers given in Table II. were taken. The values of f for positive discharge are given for three pressures:—76, 40, and 20 centim. of mercury. Those for negative discharge are only given at 20 centim. The reason being that the latter show a good deal of irregularity at higher pressures, seeming (as will be seen later) to depend largely on the condition of the point-surface, which the positive values do not. The values of f for needle C are inserted with queries, as they are almost certainly too high. The extreme fineness of its point necessitated a very rapid tapering to the sharpest part, so that a good deal of the measured pull must have been due to lines of force starting from its sides. This is borne out by the numbers in the four last columns.

TABLE II.

Needle.	r.	f.				$f \times r^{0.8}$.			
		(+) $p=76$	(+) $p=40$	(+) $p=20$	(−) $p=20$	(+) $p=76$	(+) $p=40$	(+) $p=20$	(−) $p=20$
C	$0{\cdot}7\times10^{-3}$	? 6350	? 5200	? 4600	? 3390	[19·0]	[15·6]	[13·8]	[10·1]
D	1·6 „	2850	2180	1700	1200	16·4	12·6	9·8	6·9
E	1·88 „	2450	1900	1500	1050	16·1	12·5	9·8	6·9
F	4·03 „	1400	1030	810	580	17·0	12·5	9·8	7·0
G	4·84 „	1180	870	643	510	16·6	12·2	9·0	7·1
H	6·52 „	935	680	518	405	16·6	12·1	9·2	7·2
I	7·11 „	890	630	470	380	17·0	12·1	9·0	7·3
J	7·83 „	800	585	450	360	16·5	12·1	9·3	7·4
K	8·71 „	780	560	425	320	17·5	12·6	9·5	7·2
L	10·9 „	648	450	326	290	17·4	12·1	8·8	7·8
M.....	31·8 „	335	227	152	140	21·2	14·4	9·6	8·8
N	45·7 „	308	198	130	138	26·1	16·8	11·0	11·7
O	58·0 „	302	194	132	140	30·9	19·9	13·5	18·0

In Curve IV., r is plotted with f at 76 centim. pressure, from this Table.

Now these columns show that below a point-radius of $\frac{1}{10}$ millim. f varies in close proportion with $r^{-0\cdot8}$, and they consequently negative hypothesis (*b*). But they also negative (*c*), for the pull per square centim. normal to a film of surface-tension T and radius of curvature r necessary to break it is proportional to T/r, and if this pull is to be supplied by f it follows that f^2 must be proportional to T/r, which gives $-0\cdot5$ instead of $-0\cdot8$ as the power of r with which f varies. Even $-0\cdot5$ is higher than can be assumed, for it is calculated on the supposition that there is no cohesion between the film and the point, and the existence of cohesion would still further reduce the power of r, as tending to bring the film nearer to class (*b*).

Resistance to discharge at a point is thus to be found in the surrounding gas, and is therefore practically reduced to the breaking down of Grotthuss chains, the lengths of which are not negligible compared with the radius of curvature of the point. I do not mean by this to exclude surface-resistance as a possible factor in discharge—indeed what follows shows that it may be very appreciable ; but it is not the whole, nor I believe an important part, of the resistance at a clean point.

§ 5. After a point has been used for discharge for some time its resistance greatly increases, and when discharge occurs it begins with a suddenness and violence which is very suggestive of the bursting of a film. The effect is increased if the point be now reburnished (without regrinding), though this process makes it *look* as if it had never been used. For instance, Curves II. are those connecting the pressures of the air with f for needle H. The continuous curve A B represents f at the commencement of positive discharge, C D being for negative. The readings for these two curves were taken alternately, two at a time, the pressure being gradually increased. They correspond to an unused clean needle. The cloud of points (⊙ for positive and × for negative discharge) was obtained on attempting to repeat the curves, and it was noticeable that each repetition increased the values of f, though the needle was well polished on dry wash-leather and rouge each time. Afterwards the needle was reburnished, and the dotted curves E F (+) and G H (−) obtained, showing a still further increase of f and no less irregularity in its values than before.

The above, therefore, furnishes evidence of the growth of resistance at a point when it is used. That the current does not permanently clear the formation away in getting through is obvious from the readings ; but if a reading be taken quickly after another with a point in this condition, the

second value of f is often slightly lower than the first; as if the film had not had time to finish forming again after the first discharge. Now if this were so it would follow that the value of f, when the current stops, should be less than when it starts (for a used point only; the two values agree closely for a clean one). To test this needle H was again taken and the values of f determined for various air-pressures at the point when the current just stopped, the potential of the needle being gradually diminished until a high-resistance (7000 ω) Elliot galvanometer between the needle and the earth stood at zero. The results are given in Curves III.; A B and C D for the unused point are repeated from Curves II. for comparison. J K and L M are the new curves. They are marked by circles. The agreement between J K and A B could not be closer, and points unmistakably to a *temporary* cleaning of the point while current is flowing. L M, for negative discharge, is very curious—coinciding as it does with C D at low pressures, while it leaves it so completely higher up. It was noticeable that just in proportion as the two curves diverged, the stoppage of the current was marked by increasing suddenness. At high pressures it was impossible to get the needle to discharge at all with a small current; either the flow was strong or it stopped altogether with a jerk—the same effect, though almost microscopic, being just perceptible at the cessation of positive discharge also. This being so, it follows that the values of f on the negative curve really correspond to a strong current and not to the point where the current stops. Hence their greater values. The sudden cutting off of the negative current was very striking, and suggested rather forcibly the covering over of the point by some sort of film that had been perforated by it. It is true that the positive discharge was hardly affected, but this is only an example of what has been already alluded to—the relatively greater instability of negative than of positive discharge.

Although the silent discharge from a point does not appear to have the power of permanently clearing away surface-resistance, sparks do so readily enough—though under suitable circumstances they will also form it again. In making the measurements on needle B (Table I.), the discharge at the last recorded (+) reading took the form of a spark. $\sqrt{P}$ was here 1·59. On repeating the reading it had risen to 1·95. A third discharge brought it back to 1·62, and after that it continued to oscillate between these two values for some 20 or 30 times with hardly a break in the regularity. Obviously one spark formed a resistance and the next blew it away

again. The character of the sparks was quite different too. The one which formed the resistance was thin and sharply defined, and spread out for a considerable distance over the plate like a splash. The other was much brighter, straight, and without any signs of a defined edge.

While, however, the above is evidence of the existence of surface-resistance at used points, the fact that the values of f at beginning and end of discharge are practically identical for a clean point for both positive and negative electricity, may be regarded as showing that such resistance is either very small or non-existent on points which have not been used before.

Atomic Charge.

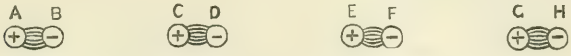
§ 6. Assuming, then, provisionally that cohesion in Grotthuss chains is the sole cause of the resistance offered to discharge at a clean point, and that gas atoms are consequently concerned in carrying the electricity when it does go*, there arises the interesting question as to the amount of charge carried by each atom; and one is tempted to see whether the above measurements throw any light on it. Without in any way pretending to settle the point, the following considerations seem to me to render it probable that the electrochemical equivalent of gas atoms is of the same order of magnitude as that of the same atoms in electrolytes.

The essence of a Grotthuss chain is that it shall consist of molecules capable of being split into two parts, one of which is charged after the split with positive electricity and the other with negative. These charges may exist separately in the molecules to start with, or they may be induced by an electrostatic field—but in either case it is the field which subsequently arranges them in chains; and the breaking down of the chains occurs when the mechanical pull of the field on the charged parts is sufficient to overcome their mutual affinity. This affinity may be due to one of two causes or their combination. Either it is (a) the electrical attraction of two initial charges, or it is (b) a cohesive attraction without any previously existing charges, or it is (c) both. One of these three it must be, if by cohesive attraction is understood the sum of all nonelectrical forces between the two parts of the molecule.

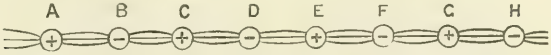
Consider the first (a) of these cases. If the molecules hold

* This does not preclude the possibility of metal dust in the discharge *after it has once started.*

together by internal charges, they may be represented thus in their free state :—

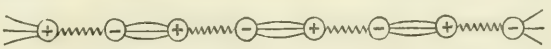


the lines between the pairs of atoms signifying lines of electrostatic force. A chain of such molecules will give way when it is put in a field of force just strong enough to redistribute the charges by induction so that half as many lines pass between A and B, C and D, &c. as before ; and the remainder pass between B and C, D and E, &c. This state of things may be represented thus :—



Put in another way, the strength of the field which will do this is rather greater than that which would induce on each of the two end atoms of the chain half their assumed initial charges, supposing them to be connected by a fine conducting wire. It depends thus on the length of the chain, being greater as the chain is shorter.

In the case (*b*), a constant cohesive affinity between the two parts of the molecule, it is necessary to suppose that electricity can pass from one to the other under the influence of induction when they are put in a field of force, in order that after separation they may be oppositely charged. The following figure shows a chain of such molecules on the point of



breaking down, the break occurring when the cohesive forces (∿∿∿) are just overcome by the electrical forces (≡) set up by the field. Here, again, the longer the chain the weaker the field required to break it ; and as the cohesive forces are constant, and the electrical forces are dependent, for given molecular arrangement, only on the charges induced in the molecules, it follows that these charges will also be practically constant, no matter what the length of the chain may be.

In both these cases, therefore, *for all lengths of chain*, the atomic charges at the breaking-point are constant ; in case (*b*) being rather less than such as would be induced by the field on the end atoms, supposing the latter to be connected by a conductor ; and in case (*a*) less than twice that amount (less, because the chain is not a continuous conductor). Their

values might thus be calculated in terms of f if the geometrical conditions were known. This, however, is not the case under the conditions of actual experiment; but by arranging that the chains shall consist of single molecules only, it is possible to get an idea of the magnitude of the charge in question. Reduce in imagination the discharging-point to molecular dimensions; and find, by what is rather violent extrapolation, the corresponding value of f at discharge from the constant in Table II. The Grotthuss chains will have been reduced to single molecules by the reduction of the point, and by supposing them to be spheres the + and − charges induced on their opposite sides may be calculated. These charges will then represent in the case of (*a*) half, and in the case of (*b*) the whole of the atomic charge.

Taking the diameter of a molecule as $\frac{1}{2}\times10^{-8}$ centim., the value of f *at the centre* of a molecule opposite the point is (from Table II.)

$$f=\frac{16{\cdot}5}{4}\times\left(\frac{1}{4}10^{-8}\right)^{-0{\cdot}8}=3{\cdot}1\times10^{7}\text{ E.S. units,}$$

which will induce on a conducting sphere of the same dimensions equal and opposite charges of

$$\frac{3}{4}\left(\frac{1}{2}10^{-8}\right)^{2}f=6\times10^{-10}\text{ E.S. units.}$$

This number is greater than the atomic charge (or than half the atomic charge) because it is calculated from measurements on chains of many molecules, which, as was pointed out above, are not conductors, but only lines of high S.I.C. Now the most probable value of the ionic charge of oxygen is 10^{-11}, which, considering the extent of the extrapolation and the fact that the above number is too great, is in sufficiently striking agreement with it. It is at any rate satisfactory that the experimental number is the larger of the two.

It is interesting to see whether a similar result is to be got from measurements of sparks between plates. Taking Dr. Liebig's numbers above referred to, I find, following Prof. J. J. Thomson, that the formula $f=\frac{a}{l}+150$ expresses the results for the smallest spark-lengths in air fairly well, considering that the numbers for that part of the curve are rather irregular. The values of a lie between 1·9 and 1·4 for the five smallest spark-lengths ($l=0{\cdot}0066$ to $0{\cdot}0245$ centim.).

Extrapolating for a distance between the plates of $\frac{1}{2} \times 10^{-8}$, the field between them comes to be 4×10^{8}. This would induce a still higher charge (8×10^{-9}) on a spherical molecule; but it must be remembered that these data are much further removed from molecular dimensions than mine.

On the other hand, there is a case accessible of what may perhaps be called discharge between plates, which takes place actually within molecular dimensions: I mean the passage of electricity at the cathode of a voltameter. Here, if a step of potential of, say, 1 volt be assumed, and if f stand for the corresponding field between the liquid and the metal of the cathode,

$$f \times \frac{1}{2} 10^{-8} = \frac{1}{300}, \quad \text{or } f = \frac{2}{3} 10^{6} \text{ E.S. units.}$$

This is capable of inducing on a spherical molecule charges of $1{\cdot}5 \times 10^{-11}$ E.S., a number which cannot be distinguished from the ionic charge. Moreover, no reduction is necessary here as the data of calculation are from measurements made direct on single molecules.

Taking, then, these three calculations together, and having regard to the fact that the nearer the conditions of experiment approach molecular arrangement the closer are the results to the value of the ionic charge, I cannot help thinking that they furnish strong grounds for supposing that electrified atoms in gases are associated with the same quantity of electricity as in electrolysis.

As regards the third possibility of molecular cohesion (*c*) mentioned above, that it is due to a combination of (*a*) and (*b*), it is impossible, without knowing the relative values of the two forces at work, to get any idea of the atomic charge from the value of f. All that can be said is that it will be less than the value calculated for atoms held together by electrical attraction only. Even in this case, therefore, there is nothing to negative the presence of ionic charges in gaseous conduction.

Effect of Pressure.

§ 7. If the conclusions arrived at above be correct, one may picture a metal point on the verge of discharging as a smooth curved conducting surface studded all over with Grotthuss chains standing up on it like bristles. The density of charge upon it will thus be far from uniform. It will reach a maximum at the root of each chain, the quantity collected there being constant for a given gas, independent of the length of the chain, and equal perhaps to the ionic charge of the gas atoms. In between the chains the density will be much less.

Now the field (f) measured by the attraction of a plate on a needle-point is the *average* number of lines of force per square centimetre of the point-surface, and takes no account of the manner in which they are distributed over it. (This is because the point is so small that the lines have room to become uniformly spread out before they reach the plate.) Hence it follows that, for different dispositions of the chains, the measured values of f may be very different, and yet the number of lines of force running through each chain be the constant number corresponding to ionic charge on its atoms. f, in fact, for a given amount of induction per chain, depends both on the length and on the closeness of the chains. Great length or great closeness, or both, means that the greater part of the lines proceeding from the point have been absorbed by the chains, hardly any passing in between them. In this case f is practically proportional to the number of chains per square centimetre and is independent of their lengths. On the other hand, very short chains, or very few to the square centimetre, or both, mean that f is sensibly independent of their closeness, but is now dependent on their length; being inversely proportional thereto so long as it is not very great compared with the radius of curvature of the point. Between these two extremes f depends both on length and on closeness of the chains—varying in an inverse manner with the former, and in a direct manner with the latter.

Now both length and closeness of the chains increase with increase of gas-pressure. Hence there must be some pressure A above which f is sensibly proportional to the closeness of the chains only, and some lower pressure B below which it is inversely proportional to the chain-lengths only. In the neighbourhood of A increase of pressure will affect f chiefly by the resulting alteration of the closeness, and will therefore increase f. Near B it will have the opposite effect, as increase in the length of the chains means a decrease of f. Hence between A and B there must be some pressure for which f is a minimum. This point is of course well known to exist*, though I was unable to obtain a sufficiently good vacuum with my apparatus to reach it. If, however, f be expressed in terms of some power (n) of the pressure, n will be 0 at the minimum point, and positive and increasing as the pressure rises from there. This increase is shown well in Table III. (calculated from Table II. for positive discharge only—the negative is too uncertain). Here n_1 is calculated from the values of f corresponding to 76 and 40 centim. of mercury, and n_2 for 40 and 20 centim. n_2 is in every case less than n_1.

* Röntgen, Wiedemann's *Electricität*, vol. iv. § 582.

TABLE III.

Needle.	r.	n_1.	n_2.
C	$0{\cdot}7\times10^{-3}$	0·31	0·20
D	1·6 „	0·42	0·36
E	1·88 „	0·39	0·34
F	4·03 „	0·48	0·35
G	4·84 „	0·48	0·44
H	6·52 „	0·50	0·39
I	7·11 „	0·53	0·42
J	7·83 „	0·49	0·38
K	8·71 „	0·52	0·40
L	10·9 „	0·52	0·46
M	31·8 „	0·61	0·58
N	45·7 „	0·69	0·61
O	58·0 „	0·69	0·56
X	400·0 „	[0·80]	0·72

The needle marked X was in reality a steel ball used for bicycle-bearings. This was put opposite a tin disk of 6 centim. diameter at a distance of 3·6 centim. n was calculated from measurements of the difference of potential between ball and plate, as f could not be measured. The values of n fit in well with the rest. (n_1 was calculated in this case from f at 40 and 60 centim. mercury.)

Now pressure alters the length and closeness of the chains at the same time; but, for a given field-strength at a point-surface, alteration in curvature gives rise to alteration of chain-length only, the length being less as the point gets sharper. Hence at a sharp point f is more dependent on the length of the chains than at a blunt one; it is in fact nearer its minimum value, and n is consequently less. This, too, is shown very clearly in Table III.

A pretty illustration of the influence of point curvature on n was accidentally met with in the case of needle C. In getting it into the apparatus for repetition of the curves obtained with it, its point came against the metal box and was flattened slightly to a width of about $3{\cdot}6\times10^{-3}$ centim. The values of n_1 and n_2 obtained from it after this were respectively 0·42 and 0·30, instead of 0·31 and 0·2 for the finer point.

Grotthuss chains, coupled with constant atomic charge, are thus well able to explain most of the phenomena described in this paper. There still remains one which is perhaps the most important of all—the difference in the behaviour of positive and negative discharge. This I hope to discuss in connexion with experiments now in progress, but it may perhaps be well to place on record the results so far obtained.

Table IV.

	r.	k.
C	$0{\cdot}7\times10^{-3}$	1·36
D	1·6 ,,	1·42
F	4·03 ,,	1·40
G	4·84 ,,	1·26
H	6·52 ,,	1·28
I	7·11 ,,	1·23
J	7·83 ,,	1·24
K	8·71 ,,	1·32
L	10·9 ,,	1·13
M	31·8 ,,	1·08
N	45·7 ,,	0·94
O	58·0 ,,	0·94
X	400·0 ,,	0·83

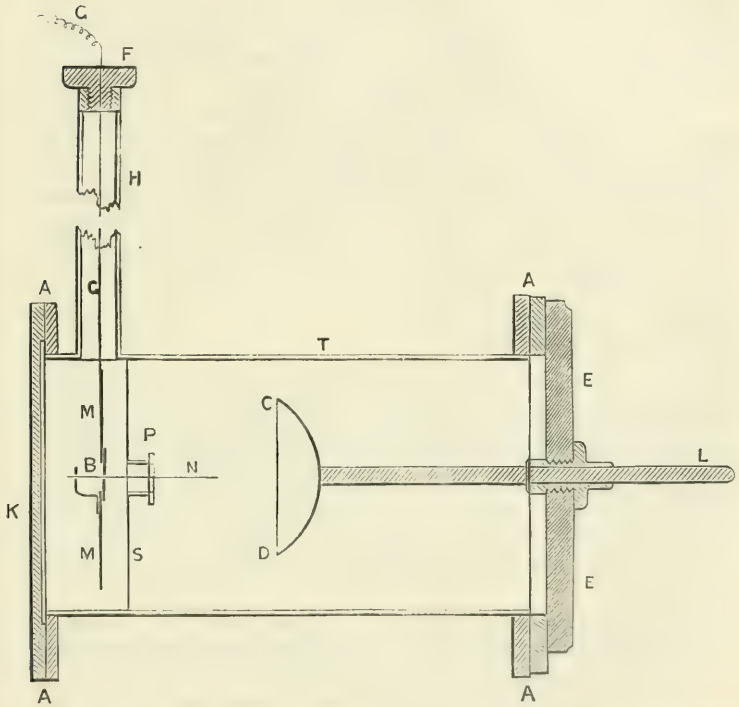
These are given in Table IV., where k is the ratio at a pressure of 20 centim. of f for positive discharge to f for negative. The ratio shows a distinct tendency to decrease as r increases. It is almost useless to give values at higher pressures on account of the uncertainty as to the condition of the point, and the great effect this may have on the negative discharge (Curves III.); but the ratio is distinctly less at higher pressures for points which seemed quite clean: the decrease of k at 70 centim. mercury varying from 3 to 8 per cent. as compared with k at 20 centim. For dirty points the decrease may reach 50 per cent.

Description of Apparatus.

§ 8. The electrometer used for potential measurements was constructed on the principle of the one designed some years ago, for absolute measurement of much smaller quantities, by Prof. Minchin. The attracted disk is suspended, and the force of attraction measured by tilting the whole instrument until the disk falls back by its weight to a fixed point. The disk is a sheet of mica, covered on one side with tin-foil and metallically connected with the case of the instrument, which is a tin cylindrical box 30 centim. long by 30 centim. diameter. The disk hangs just outside a 3-inch hole in a tin screen at one end of the case, and opposite the hole inside the case is an adjustable disk of tin which forms the attracting plate. The sensitiveness of the instrument may be varied very greatly by altering the distance between this plate and the suspended disk. This arrangement does not of course permit of absolute measurement, but it was thought that calibration in terms of spark-lengths was sufficiently accurate for the work in hand.

The same principle of tilting was used in measuring the attractions on the needle-points ; the needle in this case taking the place of the suspended disk. The zero-position was determined by a hair in the eyepiece of a microscope through which the point of the needle was observed ; the latter being at the centre of curvature of C D (fig. 1) when it coincided with the hair. The needle was illuminated by small windows in T (not shown). L was connected to the Wimshurst ; T to

Fig. 1.



T, brass tube forming body of instrument ; length 10 centim., diameter 6 centim.

H, tube for suspension-wire G. F, ebonite plug.

M, mica disk suspended from G, carrying light metal clip B holding needle N.

S, tin screen soldered into T.

K, metal cover. E, ebonite cover.

A A, ground air-tight joints, greased.

C D, spherical metal cup to be electrified ; C D = 3·35 centim., radius of curvature = 1·76 centim.

P, short brass tube on S ; length = 0·5 centim., diameter = 1·2 centim.

Point of N at centre of curvature of C D. Length of needle projecting beyond P = 2 centim.

earth; and G (*i. e.* N) through a high-resistance galvanometer to earth, the indications of the galvanometer being therefore due only to current discharged from N. A much larger instrument constructed on the same lines was used for needle A and other measurements. The body of this instrument is a tin cylinder 43 centim. long (horizontally) and 23 centim. in diameter. The needle is suspended in a small metal box at the centre, and the electrified plate is supported like C D (fig. 1) from one end.

The tilting is effected in each of the above instruments by fixing them to a brass base, provided with pivots at one end and a vertical micrometer-screw with large divided head at the other. This method works admirably.

In conclusion I wish to express my thanks to my friend Mr. F. B. Fawcett, a former student of University College, Bristol, and to my assistant Mr. J. Quick, for much careful help in carrying out the measurements described in this paper. To Prof. Lodge my thanks are so numerous that I cannot express them. His kindness, both by word and by deed, has been unceasing. Indeed but for him this paper would probably never have been written.

University College, Bristol.

XXXVII. *On the Relation between the Density and Composition of Dilute Sulphuric Acid.* *By* A. W. Rücker, *F.R.S.**

SOME time ago I had occasion to examine closely Mr. Pickering's method of detecting breaks in curves representing the results of experiments, and in consequence of the recent controversy on the subject I have lately reconsidered the matter.

Mr. Pickering's work covers a wide area, and he cannot complain if those who study his method devote themselves particularly to some one application of it.

I have specially investigated the curve which expresses between 46 per cent. and 80 per cent. the relation at 18° between the percentage strength of the solution and the "first differential" of the densities.

This was chosen on two grounds. First, because it includes within its range the percentage corresponding to the hydrate which Mr. Pickering has isolated. Secondly, because, although Mr. Pickering estimates the magnitude of the possible error of observation to be greater at 18° than at other temperatures, the agreement between his curves and

* Communicated by the Author.

the results of observation appears in this case to be freer from exceptional, and possibly accidental, causes of disturbance than in others.

I have therefore tried to find an equation which will express a considerable portion of this curve to within the limits of the error of experiment.

If a curve, determined from isolated points, is discontinuous, it is nevertheless often possible—though perhaps difficult—to express it by a moderately simple continuous equation. To do this, however, terms would have to be introduced which express the rapid change of curvature in the neighbourhood of the point of discontinuity.

My equation, however, consists of three parts, which are not suited to turning awkward corners.

The lower part of the curve is nearly a straight line. The differences between the ordinates of the upper part of the curve and those of this line are very accurately in geometrical progression.

If this were all, the equation would be of the form

$$y = a + bx - cd^x.$$

As a matter of fact, for the middle region this curve lies a little below that given by experiment. The difference gradually increases, reaches a maximum, and dies out; but the change is very gradual, extends over a considerable range, and does not in the least suggest discontinuity.

To make the two curves, given by observation and calculation, fit, I have introduced a term which makes the form of the equation

$$y = a + bx - cd^x + \frac{m}{n^x + n^{-x}}.$$

A curve of this kind has in all seven arbitrary constants, for if we change the origin to $x_0 y_0$ it may be written

$$y = a' + bx - c' \cdot d^x + \frac{mk}{n^x + k^2 n^{-x}}$$

where

$$k = n^{x_0}.$$

In the following Table I give the values of the three terms, $a + bx$, cd^x, and $m/(n^x + n^{-x})$, so that the fact that no term introduces violent and sudden changes may be obvious.

I have carried out the calculations to one place further than the results of the observations are given, as Mr. Pickering uses that place in the readings from his smoothed curve, given in Table III. of his paper (Trans. Chem. Soc., March 1890, p. 145).

The values of the constants are as follows when $x=p-61$ (p=percentage) :—

$$a=0{\cdot}010957,$$
$$b=0{\cdot}0001119,$$
$$c=0{\cdot}00006458,$$
$$d=1{\cdot}1925,$$
$$m=0{\cdot}00011,$$
$$k=1,$$
$$n=\sqrt[6]{6}=1{\cdot}348.$$

TABLE I.

($x=p-61$.)

p.	$(a+bx)\times10^6$.	$cd^x\times10^6$.	$m^{\prime}(nx+n-x)\times10^6$.	ds/dp (calculated).
80·54	13144	−2014		11130
80·04	13088	−1845		11243
79·48	13025	−1671		11354
79·12	12985	−1569		11416
78·62	12929	−1439		11490
77·11	12760	−1101	1	11660
74·98	12521	− 757	2	11766
73·01	12301	− 535	3	11769
71·06	12083	− 380	5	11708
69·10	11863	− 269	10	11604
67·12	11642	− 190	17	11469
65·51	11462	− 143	27	11346
65·12	11418	− 133	30	11315
64·50	11349	− 120	34	11263
63·08	11190	− 93	46	11143
61·01	10958	− 65	55	10948
58·94	10726	− 45	46	10727
57·94	10615	− 38	38	10615
56·89	10497	− 31	30	10496
54·89	10273	− 22	17	10268
52·91	10052	− 15	10	10047
50·91	9828	− 11	5	9822
48·91	9604	− 8	3	9599
46·94	9384	− 5	2	9381

Before comparing these numbers with Mr. Pickering's experimental results it is convenient to deduce from his Table II. the values of ds/dp given by his own smoothed curve. This can be done with fair accuracy for the greater number of points.

The following Table proves that for a large part of the curve the "second differential" at any point is to within 5

in the last place the arithmetical mean of the corresponding quantities given for two other points of which the abscissæ (p) differ by equal amounts from that of the point in question.

Thus the value of d^2s/dp^2 at 80·5 per cent. is the mean of the values at 81·5 per cent. and 79·5 per cent.

TABLE II.

p.	$\frac{d^2s}{dp^2}\times 10^6$.	Mean.	p.	$\frac{d^2s}{dp^2}\times 10^6$.	Mean.
81·5	−370		61·0	102	99
80·5	−290	−290	59·5	105	102*
79·5	−210	−215	58·5	102	105
78·5	−140	−135	57·5	105	102
77·5	− 60		56·5	102	107
76·5	− 80		55·5	110	105
75·5	− 50	− 45	54·5	108	111
74·5	− 10		53·5	112	109
73·5	− 10		52·5	110	
72·5	+ 2		51·5		
71·0	53		50·5		
69·0	61	62	49·0	111	
67·0	72	70	47·0	105	104
65·0	80	83	45·0	98	96
63·0	94	91	43·0	88	

* The difference of the two values of $ds\,dp$, from which this number is obtained, is 127. I am not sure whether this discrepancy is due to a mistake or to the supposed existence of a point of discontinuity.

The intervals from which these mean values are calculated are at least twice as great as those which have to be used in deducing values of ds/dp at points intermediate to those given. Hence the errors introduced are not likely to exceed 2 or 3 in the last place.

I have therefore deduced from the numbers in Mr. Pickering's Table II. the readings on his curves at the points corresponding to his experiments.

In the following Table III., p_0 and $\left(\frac{ds}{dp}\right)_0$ are the values of these quantities given in Mr. Pickering's Table III. The percentage at the experimental points is p, and $p_m=(p+p_0)/2$.

The second differential at p_m is calculated from my Table II. above and indicated by $\left(\frac{d^2s}{dp^2}\right)_m$, and by means of this the value of $\frac{ds}{dp}$ at p is deduced.

Thus, to give an example. If the values of $\frac{d^2s}{dp^2}$ at 80·5 per

cent. and 79·5 per cent. are −290 and −210 respectively, at 80·27 per cent.

$$\left(\frac{d^2s}{dp^2}\right)_m = -210 - 80 \times 0{\cdot}77 = -272.$$

$$\therefore \text{ Since at 80 per cent. } \left(\frac{ds}{dp}\right)_0 = 11230,$$

$$\text{at 80·54 per cent. } \left(\frac{ds}{dp}\right) = 11230 - 272 \times 0{\cdot}54$$

$$= 11230 - 147 = 11083.$$

TABLE III.

p_0.	$\left(\frac{ds}{dp}\right)_0$.	p_m.	$\left(\frac{d^2s}{dp^2}\right)_m$.	p.	$\frac{ds}{dp}$.
80	11230	80·27	−272	80·54	11083
,,	,,	80·02	−252	80·04	11220
79	11440	79·24	−191	79·48	11349
,,	,,	79·06	−179	79·12	11419
78	11580	78·31	−125	78·62	11503
70	11645	70·53	+ 55	71·06	11703
68	11523	68·55	63	69·10	11592
66	11380	66·56	74	67·12	11463
64	11220	64·75	82	65·51	11343
,,	,,	64·56	83	65·12	11313
,,	,,	64·25	85	64·50	11262
62	11033	62·54	96	63·08	11137
60	10830	60·50	103	61·01	10934
58	10602	58·47	102	58·94	10698
57	10497	57·47	105	57·94	10596
56	10395	56·44	102	56·89	10488
54	10177	54·44	108	54·89	10273
52	9955	52·45	110	52·91	10055
48	9503	48·45	109	48·91	9602
46	9293	46·47	103	46·94	9390

It remains to compare the two sets of values given by my single curve and Mr. Pickering's five curves respectively with his experimental numbers.

In doing so we must remember what the estimated experimental error is. Mr. Pickering regards the possible error in the determination of a density as $=0{\cdot}000008 = \epsilon$ say. Hence the possible error of ds/dp is $2\epsilon/\delta$, where δ is the difference between the percentages of the two points from which it is determined. In general $\delta = 2$, so that the error of ds/dp is $\pm 0{\cdot}000008$. The experiments at 18° (which are alone treated of in this paper) are supposed to be less accurate than the others, but Mr. Pickering does not think that the error of experiment reaches twice the above value*. He admits that the

* It must, however, be remembered that the 18° curve was chosen as the abnormal errors appear to be fewer and less than in other cases.

curves prove that errors do exist of larger amounts than these, especially where the two points used in calculating ds/dp were found from different solutions. I think, therefore, that I shall be expressing his views if I say that he regards the normal limit of error in the present set of experiments as $< 16 \times 10^{-6}$ and $> 8 \times 10^{-6}$, when the interval between the points used in finding ds/dp is 2 per cent. The estimated maximum error calculated on this basis is shown in the following Table :—

TABLE IV.

p.	$\frac{ds}{dp} \times 10^6$. Observed. α.	Calculated from formula. β.	Deduced from Pickering's numbers. γ.	$\beta - \alpha$.	$\gamma - \alpha$.	Maximum error estimated numerically: less than	greater than
80·54	11117	11130	11083	+13	−34	30	15
80·04	11251	11243	11220	− 8	−31	15	8
79·48	11400	11354	11349	−46	−51	32	16
79·12	11412	11416	11419	− 4	+ 7	19	10
78·62	11426	11490	11503	+64	77	43	22
77·11	11673	11660	.....	−13	...	14	7
74·98	11753	11766	.....	+13	...	16	8
73·01	11767	11769	.. ...	+ 2	...	16	8
71·06	11708	11708	11703	0	− 5	15	8
69·10	11595	11604	11592	+ 9	− 3	16	8
67·12	11467	11469	11463	+ 2	− 4	16	8
65·51	11311	11346	11343	+35	+33	26	13
65·12	11320	11315	11313	− 5	− 7	16	8
64·50	11335	11263	11262	−72	−73	41	20
63·08	11127	11143	11137	+16	+10	15	8
61·01	10936	10948	10934	+12	− 2	15	8
58·94	10731	10727	10698	− 4	−33*	15	8
57·94	10602	10615	10596	+13	− 6	7	4
56·89	10466	10496	10488	+30	+22	16	8
54·89	10275	10268	10273	− 7	− 2	16	8
52·91	10054	10047	10055	− 7	+ 1	16	8
50·91	9811†	9822	.....	+11	...	16	8
48·91	9599	9599	9602	0	+ 3	16	8
46·94	9382	9381	9390	− 1	+ 8	16	8

* This error may be due to the uncertainty as to the value of $\frac{d^2s}{dp^2}$ at this point.

† This is given in Mr. Pickering's Table I. as 982.

In studying this Table one fact must be borne in mind. The last figure in all the columns is doubtful. In order to

obtain it I have had to carry Mr. Pickering's own calculation of the value of ds/dp from his experiments to a place beyond that at which he—very properly in my opinion—stopped.

In the third column (β) the last figure is affected—in the case of the higher percentages—by the third decimal in the percentages, which I have ignored. The error thus committed is, however, small.

As regards the fourth column (γ), small errors may be introduced into the last place by the method of calculation.

If, then, we discard the last place and express each value of $\beta-\alpha$ and $\gamma-\alpha$ in terms of the number of units in the last place but one to which it most nearly approximates, we get the following Table, in which, for brevity, the values of p and signs are omitted :—

Table V.

$\beta-\alpha$	$\gamma-\alpha$	$\beta-\alpha$.	$\gamma-\alpha$.	$\beta-\alpha$.	$\gamma-\alpha$.
1	3	0	0	0	(?)
1	3	1	0	1	1
5*	5	0	0	3*	2
0	1	3*	3	1	0
6*	8	0	1	1	0
1		7*	7	1	
1		2	1	0	0
0		1	0	0	1

It is evident from this Table that, taking a broad view of the relative claims of one continuous or five discontinuous curves to represent the results, there is not much to choose between them.

There are five points (marked with asterisks) at which both systems indicate large errors. These are partly accounted for by the fact that at most of them the differences between the values of p by means of which ds/dp was calculated were unusually small. At all of them also the two points required were obtained by means of different solutions, so that sources of error not included in Mr. Pickering's estimate of the maximum affected the results.

These points Mr. Pickering regards as abnormal. I will therefore neglect them, only remarking that if sources of error of such magnitude are introduced by a change in the fundamental solution from which the mixtures are made up, similar unreckoned errors may be introduced in the process of forming the individual mixtures. An inspection of the curves at 8°, 28°, and 30° confirms this suspicion.

Omitting these points, however, the next most striking fact is that the values of $\gamma-\alpha$ are large for the two largest percentages, viz. 80·54 per cent. and 80·04 per cent. This is not a mistake. The value of $\frac{ds}{dp} \times 10^6$ at 80 per cent. is given in Mr. Pickering's Table III. as 11230, and the numerical value of ds/dp diminishes as p increases. The observed value at 80·04 per cent., 11251, must therefore necessarily be a great deal too large.

If, then, we omit the abnormal points (marked with asterisks) and confine ourselves to those for which I have been able to calculate $\gamma-\alpha$, we find that, out of 14 points, errors of appreciable magnitude (to this order of approximation) occur eight times when my curve is used and seven times when Mr. Pickering's five curves are employed; the sum of the errors in the first case is 9 and in the second 11.

For my own part I think this result is sufficient to show that, in attempting to discriminate between representations of the experiments under consideration, Mr. Pickering is dealing with quantities less than the error of experiment.

The same conclusion is supported by a study of Table IV., if we admit that figures in the last place are trustworthy.

It is evident that my own results in the column $\beta-\alpha$ could be a little improved. Positive errors are the more numerous, and to make positive and negative errors balance we should have to subtract 2 from all the figures in that column. Hence it would have been better to choose for the constant a the value 0·010955 instead of 0·010957. I have not thought it worth while to rewrite the Tables to introduce this small correction.

The only point that I can see in Mr. Pickering's favour is that, if we omit the points at 80·54 per cent. and 80·04 per cent., and if we omit the points which I have called abnormal at which the errors are large, the errors obtained from his curves are kept more nearly within the limit 0·000008 than in the case of those obtained by myself.

I do not press the point that the maximum error in this case is admittedly larger than 0·000008, but I must insist that it is extremely unlikely that errors so large as those at the abnormal points exist, and that there are none larger than the estimated amount elsewhere.

Why, for instance, are we to admit an error of 22, or three times the lower limit to the maximum error, at 56·89 per cent., and insist that an error of 16, which is only twice the same limit, is impossible at 63·08 per cent.? If we do make this extremely improbable assumption, it is of course possible to reduce the errors thus arbitrarily picked out by making the curve discontinuous.

Thus, if between 53 and 58 we suppose the terms

$$\{12-5(p-53)\}\times 10^{-6}$$

to be added to the equation, the calculated values from 53 to 58 become

10059, 10270, 10488, and 10602,

which make the values of $\beta-\alpha$

5, −5, +22, and 0.

These are about of the same magnitude as the corresponding values of $\gamma-\alpha$, and, except at the abnormal* point, are less than 0·000008.

Why the large difference matters so little and the small differences are so important I do not know, but it appears to me that Mr. Pickering has been performing with a ruler an operation analogous to that I have here performed by modifying a formula.

It is, however, possible to perform the same operation over other ranges. Thus, taking the percentages in round numbers, and subtracting from the part of the curve between 65 and 54 terms given by

$$\{1+2\cdot6(60-p)^2\}\times 10^{-6},$$

we get the numbers in the following Table :—

p.	Correction term.	$\frac{ds}{dp}$	$\beta-\alpha$.
63	−24	11119	−8
61	− 4	10944	+8
59	− 4	10723	−8
58	−11	10604	+2
57	−24	10472	+6

The tenths of a per cent. omitted might affect the last figures to the extent of one unit ; but the Table proves that it is possible by such devices to bring even the point at 56·89 per cent. into line with those near to it to within limits which are admittedly less than the error of experiment. A group of points from 64 to 74 per cent. shows errors no larger than Mr. Pickering's from 59 to 71 per cent. Such a method of treating the results, whether the instrument be a ruler or a formula, appears to me unjustifiable.

There is no doubt that the larger differences between obser-

* It must be remembered that Mr. Pickering does not apply this term to these points, though he appears to regard them as exceptional.

vation and calculation are really due to errors. They occur in two instances, at all events, in pairs having opposite signs. One of these is near 79 per cent., the other near 65 per cent. They are precisely what might be expected if from any cause one density was more than usually erroneous. Is it not likely that other minor errors are to be explained in a similar way?

Mr. Pickering appears to me to be on the horns of a dilemma. If we assume the larger values of the maximum error to be correct, then the values of $\beta-\alpha$ are for the most part (except at the abnormal points) so well within the limits of the error of experiment that the whole discussion resolves itself (even from his point of view) into a controversy about matters less than the error of experiment. If the lower limit is adopted, then he must explain why, when at 64·50 per cent. the value of $\gamma-\alpha$ is some three and a half times greater than the estimated maximum error, the theory of discontinuity is required to account for the much smaller discrepancies found elsewhere.

Horizontal lines are drawn in Table IV. at the points where Mr. Pickering believes that there are breaks in the continuity of the curve. The differences $\beta-\alpha$ show no sign of regularity in these intervals, they are for the most part of the same order of magnitude as the estimated error of experiment; and any argument which could be drawn from the fact that they exceed the lower values which may be assigned to it is neutralized by the fact that in some cases they unquestionably exceed the largest limits Mr. Pickering has specifically mentioned. Finally, to obtain the last place it has been necessary to strain the calculations, and to carry them in some instances to a place further than Mr. Pickering himself has done. If therefore we adopt the safer course of neglecting figures $<10^{-5}$, the continuous equation expresses the facts at least as well as the five discontinuous curves.

It is of course logically open to Mr. Pickering to claim that his case is not disproved until a process similar to that which I have adopted has been successfully applied in a much larger number of instances. So far as I am concerned I can only reply that I think my result places him in the position of having to prove a negative, and that I certainly cannot undertake to devote myself to the multiplication of such evidence.

I have before stated that I think that the curves in some parts—if not discontinuous—have peculiar features which suggest special physical causes. Thus between 84 and 94 per cent. they are obviously nearly straight lines. My doubts have always had reference to the minor changes of curvature and to the use of the ruler in detecting them. They are confirmed by the above investigation.

XXXVIII. *Note on the Theory of the Solitary Wave.* By Sir G. G. Stokes*.

In a paper on the Solitary Wave by Mr. J. McCowan, printed in the July number of the Philosophical Magazine, for a copy of which I am indebted to the kindness of the author, he refers to a conclusion which I advanced in a paper written long since, and reprinted full ten years ago, according to which a solitary wave could not be propagated without change of form. As I have known for the last ten years that this conclusion was erroneous, and have published a paper in which the motion of a uniformly propagated solitary wave was considered, I am not concerned to defend it; but it may be well to point out the true source of the error, respecting which I cannot agree with Mr. McCowan.

While the first volume of my Collected Papers was going through the press, I was led to the conclusion (see p. 227) that the highest possible waves of the oscillatory kind (the motion being irrotational) presented a form in which the crests came to wedges of 120°. On reflecting on the application of this to very long waves propagated in water of which the depth is small compared with the length of wave, I was led to perceive that the conclusion above mentioned was erroneous, and also that the source of the error was that it was not sufficient, even though a solitary wave were very long, to treat it as indefinitely long, and consequently to take the horizontal velocity as the same from the surface to the bottom. On speaking on the subject to Lord Rayleigh, he referred me to the previous papers on the solitary wave by M. Boussinesq and himself, with which I was not at the time acquainted. The conclusion of a supplement to my paper on oscillatory waves, which forms the last article in vol. i., shows that I was then fully alive to the possibility of the propagation of a solitary wave without change; and in a short paper entitled "On the highest wave of uniform propagation (Preliminary notice)," read before the Cambridge Philosophical Society in 1883, and printed in the Proceedings (vol. iv. p. 361), I have indicated a new method, depending on a process of trial and error, for determining numerically the circumstances of uniform propagation of waves, whether of the oscillatory or solitary class, more especially in the extreme case in which the crest comes to a wedge of 120°, so that the wave is on the point of beginning to break.

I cannot agree with Mr. McCowan either that the form of expansion which I used is inadmissible, or that the form which he proposes at p. 58 to substitute, that of a series involving exponentials in which the coefficient of x in the index is

* Communicated by the Author.

real, is (at least for my purpose) admissible. It is not true that a non-periodic function of x cannot be expressed by means of periodic functions; for example, the non-periodic function e^{-x^2} may be expanded in the definite integral

$$e^{-x^2} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-\alpha^2} \cos 2\alpha x \, . \, d\alpha,$$

each element of which is periodic. On the other hand, the form of expansion proposed by Mr. McCowan is (at least for my purpose) inadmissible, on account of the discontinuity of the expression.

I will now mention more particularly the step which led me to a wrong conclusion. It is easily shown that in a very long wave propagated in water the depth of which is small compared with the length of the wave, the horizontal velocity is nearly the same from the bottom to the surface for any vertical section of the wave made by a plane perpendicular to the direction of propagation. For a given depth of water and maximum height of wave, this is so much the more nearly true as the length of the wave is greater. The horizontal velocity tends indefinitely towards constancy from top to bottom as the length of the wave increases indefinitely. Now Sir George Airy has shown that for a wave in which we may suppose the particles in a vertical plane to remain always in a vertical plane, as they must do if the horizontal velocity is the same from top to bottom, the form of the wave must gradually change as it progresses. It might seem therefore that, however small we take the height of a wave at the highest point, we have only to make the wave long enough and Airy's investigation will apply, and the wave will change its form in time as it travels along. Now in the solitary wave of Russell, the lower the wave, the longer it is; and therefore it might seem as if we had only to make the wave low enough and long enough and the length would be so great that Airy's investigation would apply, and the form would change, though slowly.

The answer to this is that, however small we take the height, we are not at liberty to increase the length indefinitely. There is in fact a relation between the height and the length in a solitary wave which can be propagated uniformly, which, though it is of such a nature that the length becomes infinite when the height becomes infinitely small, nevertheless forbids us for a given height, however small, to increase the length indefinitely.

The possibility of the existence of a solitary wave of uniform propagation is so far established by my investigation relating to oscillatory waves, as that it is made to depend on the principle that the infinite series by which the circumstances of the

motion of oscillatory waves is expressed must remain convergent until the height is so far increased that the outline presents a singular point, namely the wedge of 120°. If this be conceded, we have only to make the wave-length (in the sense of the distance from crest to crest, not in that of the distance from the point where one of the swells begins to where it ceases to be sensible) infinite, in order to pass to the case of a solitary wave uniformly propagated.

XXXIX. *Notices respecting New Books.*

(i.) *A Treatise on Trigonometry.* (Fifth edition, pp. viii+160.)

(ii.) *A Treatise on Algebra.* (Second edition, pp. viii+412.)

(iii.) *Logarithmic Tables.* (Third edition, pp. 96.)

THESE are three works, (i.) and (ii.) written by Profs. Oliver, Wait, and Jones, of Cornell University, and (iii.) arranged by the last-named gentleman, who has recently been on a visit to this country with a view, we believe, to the preparation of a new edition of the Tables. (i.) is an excellent practical treatise on both Plane and Spherical Trigonometry. "After eight years' use in the class-rooms the book has been wholly rewritten." The aim in the revision has been to make the book "simpler and more attractive as a text-book, and to make it more thorough and exhaustive as a treatise." The new matter is thus noticed:—(1) Applications of Trigonometry to surveying, astronomy, and navigation. (2) The extension of the notion of directed lines, and the introduction of such other conventions, particularly of directed surfaces, as help to interpret algebraic symbols by geometric magnitudes, and thus to lay the foundation for the study of mathematical physics. (3) The discussion of the general triangle, plane and spherical. There is no lack of admirably drawn figures, and often the same principle is illustrated by several figures: when this is the case, "the first figure is easiest followed: the others help the reader to see the generality of the principle and of the proof." The text is concise without being obscure. "Only the main lines of the subject are developed; collateral matters are outlined in the examples and left for the student to work out for himself." The authors have freely used English text-books as well as American ones, and largely drawn upon Senate-House Examination-papers. It is a work especially adapted for practical students. There is a copious Index of reference.

(ii.) This edition appears to be almost, if not quite, identical with the first edition, which we commended some few years since in our Magazine.

(iii.) is a very handy collection of most useful Tables. There is an explanation of the Tables at the end of the work, and on the title-page there is the promise of a dollar for the first notice of every error in the Tables.

The same three writers promise a text-book in Algebra whose definitions and statements of principles are *clear* and *precise*, and whose proofs are *rigorous* and so *simple* that any diligent pupil can read it

easily. The title is "A Drill-book in Algebra." The authors are the publishers of their works, which are well printed and sold at a low price. Those we have noticed above are excellent of their kind, and are evidently written by men who are experienced in teaching young men of ordinary ability.

The Number-System of Algebra treated Theoretically and Historically. *By* HENRY B. FINE, *Ph.D.* (Boston and New York: Leach, Shewell, and Sanborn; pp. x+131.)

WE simply call attention to this small work, which presents in a readable form much of what is given in the larger works of Hankel (*Complexe Zahlensystemen*), M. Cantor (*Vorlesungen über die Geschichte der Mathematik*), Weierstrass, Thomæ, and other Continental writers on the nature of the number-concept and the number-system of Algebra. The discussion follows the same lines, in the main, as the author's previous pamphlet 'On the Forms of Numbers arising in Common Algebra.'

A Treatise on Plane Trigonometry. *By* E. W. HOBSON. (Cambridge: University Press, 1891; pp. xvi+356.)

THE gratification we have derived from a perusal of this work is akin to that we felt on reading Chrystal's 'Algebra.' The thoroughness and yet withal the freshness with which our author has treated his subject puts his book in the first rank of Mathematical publications lately issued by the University Press. The theory of the circular functions is treated from the modern point of view, and yet the elementary parts are worked out in sufficient detail for students "whose range of reading is to be more limited" than that of those readers to whom the work is primarily addressed. It is pre-eminently a strong book, and will be of prime value to advanced University men, who will find the principles of the theory of Complex Quantities clearly discussed in a manner similar to that of the 'Algebra' above referred to. Even in the most recent works Analytical Trigonometry "has been too frequently presented to the student in the state in which it was left by Euler, before the researches of Cauchy, Abel, Gauss, and others had placed the use of imaginary quantities, and especially the theory of infinite series and products, where real or complex quantities are involved, on a firm scientific basis." There are eighteen chapters in all.

In a short chapter (II.) the method of projections is introduced, and this method is subsequently effectively used in conjunction with the definitions of the circular functions employed by De Morgan (see 'Double Algebra'). These definitions appear to the author to be "those from which the fundamental properties of the functions may be most easily deduced in such a way that the proofs may be quite general, in that they apply to angles of all magnitudes. It will be seen that this method exhibits the formulæ for the sine and cosine of the sum of two angles, in the simplest light, merely as the expression of the fact that the projection of the hypothenuse of a right-angled triangle on any straight line in its plane is equal to the sum of the projections of the sides on the same line." The periodicity of these functions is clearly shown,

and some space is given to their graphical representation. We then have (IV.) the addition and subtraction formulæ for functions of two or more angles, and (V.) the functions of submultiple angles. The next chapter (VI.) is to our mind the most valuable of the elementary chapters for readers for Scholarship papers. The collection of worked-out examples will be of material use to such readers on account of the many beautiful artifices used in their solution. At a somewhat earlier stage than is usual, Mr. Hobson discusses (VII.) the expansion of functions of multiple angles. He does so because "they are merely algebraical consequences of the addition theorems." In VIII. and IX. the reader is introduced to the relations between the circular functions and circular measure of an angle and the formation of Trigonometrical Tables, it being assumed at this latter stage that the student has acquired a knowledge of logarithms from some work on Algebra

Properties of triangles and quadrilaterals occupy chapters X., XI., XII. These are treated in some detail, references to the modern geometry of the triangles being in the main purposely excluded.

The Analytical side of the subject occupies chapters XIII. to the end. In XIII. is an account, with applications, of complex quantities, which is preliminary to the (perhaps) distinctive feature of Mr. Hobson's book—the rigorous discussion of the theory of infinite series. The corresponding portion in Mr. Hobson's *Encyc. Brit.* article has recently elicited commendation from Prof. Chrystal, and the work before us, we believe, presents the proofs in even fuller detail.

The exponential function, and what the author calls the "generalized logarithm" ("the doubly infinite series of values of the logarithm of a quantity"), form the subject-matter of XV.; hyperbolic functions of XVI.; infinite products of XVII.; and the closing chapter gives a proof of the irrationality of π, with other applications of continued fractions to the subject. We have noted few errors: p. 83, line 4, for h read b; p. 103, line 4, *for* (29) *read* 40 which depends on (29) of § 49; p. 123, line 15, *for second* $\sin\theta$ *read* $\tan\theta$; p. 132, line 7 up, *for* (7) *read* (11); p. 311, line 10 up, *for* $\sin(x-iy)$ *in denominator read* $\cos(x-iy)$. There is a beautiful and numerous collection of exercises which will interest any one who has a taste for the subject. The figures and the "get up" are all that one could wish for.

XL. *Intelligence and Miscellaneous Articles.*

EDITORIAL NOTE ON MR. PARKER'S PAPER ON THE ABSURDITY OF DIAMAGNETISM.

IF I had seen Mr. Parker's paper in last month's Philosophical Magazine before publication, I would have referred it back to him for some important alterations. I could hardly, however, have foreseen, when publishing a paper by a Fellow of St. John's College, Cambridge, that it was likely to contain such statements as, 1st, that there is anything new in the theory that diamagnetic action is really due to the paramagnetism of the air; and, 2nd, that no theory of dia-

magnetic action has been propounded. This "new theory" is at least as old as Becquerel (1850), and has been investigated by almost everybody who has worked at diamagnetism, and they are practically unanimous in the conclusion that diamagnetic actions *cannot* be explained by the paramagnetism of the air.

These undisputed experiments prove that such a theory as Becquerel's would require a vacuum to be paramagnetic. This is a new nomenclature, and does not make the old one absurd; it involves practically what Mr. Parker says is non-existent, namely one of the theories of diamagnetism. But all this is too well known to be worth wasting words on.

As to the second curious statement of Mr. Parker's, namely that no theory of diamagnetism exists, that is equally extraordinary. Chapter xxii. of Maxwell's pretty generally known Treatise is headed "Ferromagnetism and Diamagnetism explained by Molecular Currents," and gives an interesting description of Weber's theory of Diamagnetism in § 838. If Mr. Parker had exercised his ingenuity in explaining how Weber's theory, which, being a possible theory can be reconciled with Thomson's difficulty, it would have been more instructive than a dissertation on the absurdity of what undisputed experiments show to be real. If the opportunity had arisen, it would have been only kind to Mr. Parker to have referred the paper back to him for reconsideration before publishing it. GEO. F. FITZGERALD.

ON HOMOLOGOUS SPECTRA.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN, Cardiff, August 20, 1891.

Will you kindly allow me to say a few words in reply to the recent article by Professor Hartley in your Magazine (April 1891), which referred almost entirely to a previous paper of mine.

I regret that, in reading Professor Hartley's papers on Homologous Spectra, I failed to see his statement concerning the importance of noticing the *physical* properties of the lines of the various spectra. In comparing, however, the lines of magnesium and zinc, which he considers to be homologous, I saw at the most only the faintest resemblance. This may be due to the fact that the photographs which I used were of the arc-spectra, while his were of the spark-spectra. I had sets of both at my disposal; but the arc-spectra ones were so superior in every way that I selected them. As I said in my previous paper, I think the arc-spectrum photographs are preferable in looking for homologous lines; not because the spark-spectrum is variable, as Professor Hartley thinks I meant, but because of uniformity of conditions, sharpness of lines, freedom from haziness, &c. It may be that the difference between the arc-

and the spark-spectrum is merely one of temperature; but so far surely the arc-spectra photographs have been more suitable for the comparison of spectra. Regarding magnesium and zinc, I must still say that the resemblance is much less marked than between zinc and cadmium; and it is well to note that the recent work of Kayser and Runge shows conclusively that magnesium is not related so closely to zinc and cadmium as it is to barium and the elements on the other side of the second column of Mendelejeff's table.

Very respectfully yours,
JOSEPH SWEETMAN AMES.

Johns Hopkins University.

MAGNETO-OPTIC PHENOMENON.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN, Delft, June 23, 1891.

Having read in the Philosophical Magazine for April 1891 a translation, by Mr. James L. Howard, of a paper of mine in Wiedemann's *Annalen*, I venture to make some remarks on this translation, the exactness of which is highly to be admired. I hope that you will find occasion to correct these small errors in a following Number in order to prevent misapprehension. The first and seventh apply to misprints which have also crept into the German translation and which are corrected in Wiedemann's *Annalen*, vol. xliii. p. 680.

I am, Gentlemen,
Your obedient servant,
R. SISSINGH,
Lecturer on Physics at the Polytechnic Institute at Delft.

Page 294, line 2 from top, *for* does not pass *read* passes.
— 296, end of footnote, *for* perpendicular to the plane of incidence *read* perpendicular to the polarizer.
— 298, last line of text, *for* round the edge of a circular platform *read* longitudinally upon an iron frame.
— 299, lines 17 and 18 from top, *for* these two lines *read* inserted, just as in the case of the polarizer, on a pillar, which can be moved on a cross-piece along the frame.
— 300, line 14 from top, *for* inclined to each other *read* inclined to its length.
— 302, line 5 from top, *read* whose mean value was approaching to zero.
— 308, line 11 from foot, *for* square centimetres *read* square millimetres.
— 308, line 5 from foot, *for* the differences were $\frac{1}{2}$ wave-lengths *read* the differences were reduced to one half from one angle to the next.
— 311, line 5 from foot, *for* derived from *read* assumed in the

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

OCTOBER 1891. PM 32 (1891)

XLI. *On the Discharge of Electricity through Exhausted Tubes without Electrodes.* By J. J. THOMSON, *M.A., F.R.S., Cavendish Professor of Experimental Physics, Cambridge.**

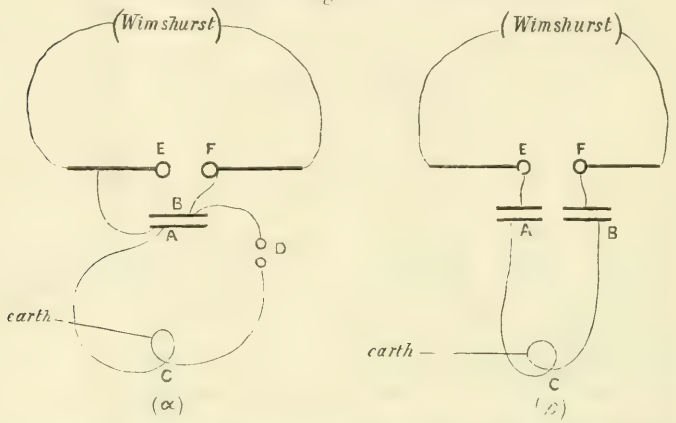
THE following experiments, of which a short account was read before the Cambridge Philosophical Society last February, were originally undertaken to investigate the phenomena attending the discharge of Electricity through Gases when the conditions are simplified by confining the discharge throughout the whole of its course to the gas, instead of, as in ordinary discharge-tubes, making it pass from metallic or glass electrodes into the gas, and then out again from the gas into the electrodes.

In order to get a closed discharge of this kind we must produce a finite electromotive force round a closed circuit, and since we cannot do this by the forces arising from a distribution of electricity at rest, we must make use of the electromotive forces produced by induction. To break down the electric strength of the gas such forces must be very intense while they last, though they need not last for more than a short time. Forces satisfying these conditions occur in the neighbourhood of a wire through which a Leyden jar is discharged. During the short time during which the oscillations of the jar are maintained enormous currents pass through the wire, and as with a moderate-sized jar these currents change their direction millions of times in a second.

* Communicated by the Author.

the electromotive force in the neighbourhood of the wire is exceedingly large. To make these forces available for producing an electrodeless discharge, all we have to do is to make the wire connecting the coatings of the jar the primary of an induction-coil of which the discharge-tube itself forms the secondary. The arrangements which I have employed for this purpose are represented in the accompanying diagram.

Fig. 1.



In (α) A is the inside coating of a Leyden jar : this is connected to E, one of the poles of a Wimshurst electrical machine, or an induction-coil, the other pole F of the machine being connected to B the outer coating of the jar. A C D is a wire connected to the inner coating of the jar, a few turns C (which we shall call the primary coil) are made in this wire ; these turns are square if the discharge-tube is square, circular if the discharge-tube is a spherical bulb. The wire at D is attached to an air-break, the other side of which is connected with the outer coating of the Leyden jar. The knobs of this air-break ought to be kept brightly polished. The loop C is connected to earth. The discharge-tubes, which were in general either rectangular tubes or spherical bulbs, were placed close to the turns of C. When the difference of potential between A and B is sufficiently large, a spark passes across the air-break, and the electrical oscillations set up produce a large electromotive force in the neighbourhood of the coil, sufficient under favourable circumstances to cause a bright discharge to pass through the vacuum-tubes. In some experiments the jars, at the suggestion of Prof. Oliver Lodge, were connected up differently, and are represented by (β) in

fig. 1. Two jars were used, the outside coatings of which, A and B, were connected by the wire containing the primary coil C. the inside coating of the first jar was connected to one pole of the Wimshurst, that of the second to the other. With this method of arranging the jars no air-space is required, as the sparks pass between the terminals of the machine, and the polishing of these terminals is not nearly so important as that of the knobs of the air-break in the arrangement (*x*).

Before proceeding to describe the appearance presented by the discharge, I will mention one or two points which may prove useful to any one who wishes to repeat the experiments. According to my experience the discharge is more easily obtained in bulbs than in square tubes, and with a Wimshurst machine than with an induction-coil. If an induction-coil is used a break which will transmit a large current ought to be substituted for the ordinary vibrating one supplied with such instruments. It is essential to success that the gas in the bulbs or tubes should be quite dry and at a suitable pressure; there is a pressure at which the brilliancy of the discharge is a maximum, and as in endeavouring to get at this pressure the exhaustion may be carried too far, it is convenient to use a form of mercury pump which will allow of the easy admission of a little gas; the pattern which I have used and found to answer very well is called the Lane-Fox pattern. When any gas is introduced it should be sent through sulphuric acid to get rid of any moisture that may be in it. Owing, I think, to the pressure in ordinary incandescent lamps being very different from that at which the discharge has its maximum brilliancy, I have met with very poor success in attempts to produce these discharges in already exhausted tubes such as incandescent lamps, though I have tried a considerable number by different makers; on the other hand, the radiometers which I have tried allow the discharge to pass pretty readily, though it is interfered with by the vanes, and is not comparable in brilliancy with that obtained in home-made tubes and bulbs. I have obtained sparks easily with apparatus of the following dimensions: two gallon jars, the outside coatings connected by a wire about 2 yards long, the coil consisting of three or four turns, each about 3 inches in diameter. I have some bulbs which with this apparatus will give a bright discharge when the distance between the terminals of the Wimshurst is only $\frac{1}{4}$ inch: these are, however, exceptionally good: it more frequently takes a spark an inch or an inch and a half long to produce the discharge.

I find that Hittorf in Wiedemann's *Annalen*, xxi. p. 138,

describes the light produced in a tube round which the wire connecting the coatings of a Leyden jar is twisted; the luminosity in Hittorf's experiments seems to have filled the tube, and not, as in the experiments described in this paper, been confined to a ring. It seems possible that the difference in the appearance in the tubes may have been due to the existence of an electrostatic action in Hittorf's experiments, the primary coil getting raised to a high potential before the discharge of the jar, and inducing a distribution of electricity over the inside of the glass of the tube; on the passage of the spark the potential of the primary coil will fall, and the electricity on the glass redistribute itself; to effect this redistribution it may pass through the rarefied gas in the discharge-tube and produce luminosity.

In my experiments I took two precautions against this effect: in the first place I connected the primary coil to earth, so that its potential before discharge took place was unaltered, and as an additional precaution I separated the discharge-tube from the primary by a cage made of blotting-paper moistened with dilute acid; the wet blotting-paper is a sufficiently good conductor to screen off any purely electrostatic effects, but not a good enough one to interfere to an appreciable extent with the electromotive forces arising from rapidly alternating currents. In this way we can screen off any electrostatic effects due to causes which operate before the electrical oscillations in the jars begin; when once these have commenced, there ought not, I think, to be any separation of the electromotive forces into two parts, one being called electrostatic, the other electrodynamic. As this is a point on which it is desirable to avoid any misunderstanding, I hope to be excused if I treat it at some length.

In the mathematical treatment of the phenomena of the "Electromagnetic Field," it is customary and not inconvenient to regard the electromotive force as derived from two sources, or rather as consisting of two parts, one part being calculated by the ordinary rules of electrostatics from the distribution of electricity in the field, the other part being the differential coefficient of the vector potential with respect to the time. From a mathematical point of view, there is a good deal to be said for this division; the two forces have very distinct and sharply contrasted analytical properties. Thus the electrostatic force possesses the property that its line-integral taken round any closed curve vanishes, while the surface-integral of its normal component taken over a closed surface does not in general vanish. The "vector potential force," on the other hand, does not in general vanish when integrated

round a closed curve, the surface-integral of its normal component taken over any closed surface, however, vanishes. When, however, our object is not so much mathematical calculation as the formation of a mental picture of the processes going on in the field, this division does not seem nearly so satisfactory, as the fundamental quantities concerned, the electrostatic and vector potentials, are both of considerable complexity from a physical point of view. We might judge that this division of the electromotive force into two parts, the one derivable from an electrostatic, the other from a vector, potential, is rather a mathematical device than a physical reality, from the fact which I pointed out in a report on Electrical Theories (B. A. Report, 1886), that though the electrostatic potential satisfies the mathematical condition of being propagated with an infinite velocity, the total electromotive force in the electromagnetic field travels with the velocity of light, and nothing physical is propagated at a greater velocity.

In an experimental investigation such as that described in this paper it is not so important that our method of regarding the phenomena should lead to the shortest analysis as that it should enable us to picture to ourselves the processes at work in the field, and to decide without much calculation how to arrange the experiments so as to bring any effect which may have been observed into greater prominence.

The method which I have adopted for this purpose is the one described by me in the Philosophical Magazine, March 1891, and which consists in referring everything to the disposition and motion of the tubes of electrostatic induction in the field. These tubes are either endless, or have their ends on places where free electricity exists, every unit of positive electricity (the unit being the quantity of electricity on the atom of a univalent element) being connected by a unit tube to a unit of negative electricity, the tube starting from the positive electricity and ending on the negative. At any point in the field the electromotive intensity varies as the density of the tubes of electrostatic induction at that point. When the electricity and the tubes in the field are at rest, the tubes distribute themselves so that the electromotive intensity at any point is derivable from a potential function; as soon, however, as the equilibrium is disturbed, the tubes move about and get displaced from their original positions, the disposition of tubes and therefore the electromotive intensity are changed, and the latter will no longer be derivable from a potential function, and according to the mathematical theory would be said to include forces due to electrostatic and electromagnetic induction. According to our view,

however, the cause of the electromotive intensity is the same in both cases, viz. the presence of tubes of electrostatic induction, and the electromotive intensity ceases to be derived from a potential, merely because the distribution of these tubes is not necessarily the same when they are moving about as when they are in equilibrium. It is shown, in the paper already referred to, that these tubes when in motion produce a magnetic force at right angles, both to their own direction and to that in which they are moving, the magnitude of the force being 4π times the product of the strength of the tube, the velocity with which it is moving, and the sine of the angle between the direction of the tube and its direction of motion. In an electric field in which the matter is at rest, these tubes when in motion move at right angles to themselves with the velocity "v," that at which electrodynamic disturbances are propagated through the medium. We can easily show that, K being the specific inductive capacity of the medium, the line-integral of $4\pi/\mathrm{K}$ times the density of these tubes taken round a closed circuit is equal to the rate of diminution of the number of lines of magnetic induction passing through the circuit. Thus, since the fundamental laws of electrodynamic action, viz. Faraday's law of induction and Ampère's law of magnetic force, follow from this conception of the field as produced by tubes of electrostatic induction moving at right angles to themselves with the velocity "v," and producing a magnetic force at right angles both to their own direction and to that in which they are moving, and proportional to the product of the strength of the tube and its velocity, it is a conception which will account for all the known phenomena of the field. It furnishes in fine a geometrical instead of an analytical theory of the field. It will also be seen that from this point of view the magnetic force, when introduced to calculate the electromotive forces arising from induction, logically comes in as an intellectual middle-man wasting mental effort.

We may thus regard the distinction between electrostatic and electromagnetic electromotive forces as one introduced for convenience of analysis rather than as having any physical reality. The only difference which I think could be made from a physical point of view would be to define those effects as electrostatic which are due to tubes of electrostatic induction having free ends, and to confine the term electromagnetic to the effects produced by closed endless tubes. It is only, however, when the electromotive forces are produced exclusively by the motion of magnets that all the tubes are closed; whenever batteries or condensers are used, open tubes are present in the field.

It will be useful to consider here the disposition and motion of the tubes of electrostatic induction in the arrangement used to produce these electrodeless discharges. We shall take the case where two jars are used, as in β, fig. 1, as being the more symmetrical.

Just before the discharge of the jar, the tubes of electrostatic induction will be arranged somewhat as follows :— There will be some tubes stretching from one terminal of the electric machine to the other; others will go from the terminals to neighbouring conductors, the table on which the machine is placed, the floor and walls of the room, &c. The great majority of the tubes will, however, be short tubes passing through the glass between the coatings of the jars. Let us now consider the behaviour of two of these tubes, one from the jar A, the other from B, when a spark passes between the terminals of the machine. Whilst the spark is passing these may be regarded as connected by a conductor; the tubes which originally stretched between them now contract, the repulsion they exerted on the surrounding tubes is destroyed so that these now crowd into the space between the terminals, the two short tubes under consideration now taking somewhat the form shown in fig. 2. These tubes being of opposite sign

Fig. 2.

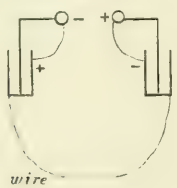


Fig. 3.

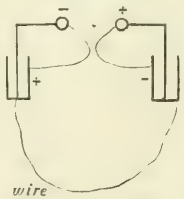


Fig. 4.

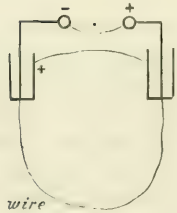
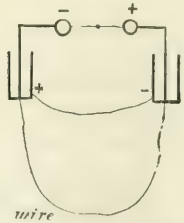


Fig. 5.



tend to run together; they do so until they meet as in fig. 3, when the tubes break up as in fig. 4, the upper portion running into the spark-gap, where it contracts, while the lower

portion rushes through the dielectric to discharge itself into the wire connecting the coatings of the jars, an intermediate position being shown in fig. 5. These tubes while rushing through the dielectric produce, as already stated, magnetic forces; some of them on their way to the discharging wire will pass through the discharge-tube; if they congregate there in sufficient density, discharge will take place through the rarefied gas.

The discharge of the jar is oscillatory, and we have only followed the motion of the tubes during a part of the oscillation; when, however, this tube enters the wire between the jars a tube of opposite kind emerges from it: the same thing happens when the other portion enters the spark-gap. These go through the same processes as the tubes we have followed, but in the reverse order, until we get again two short tubes in the jars, but opposite in sign to the original ones: the process is then repeated and so on as long as the vibrations last.

In order to see what are the most advantageous dimensions to give to our apparatus, let us consider on what the maximum electromotive force in the secondary depends. Let us take the case of a condenser of capacity C discharging through a circuit whose coefficient of self-induction is L: then, if the potential difference between the plates of the condenser is initially V_0, the current γ at the time t is (supposing as a very rough approximation that there is no decay in the vibrations) given by the equation

$$\gamma = \frac{CV_0}{\sqrt{LC}} \sin \frac{t}{\sqrt{LC}}.$$

The rate of variation of this, $\dot{\gamma}$, is therefore

$$\frac{V_0}{L} \cos \frac{t}{\sqrt{LC}}.$$

So that if M is the coefficient of self-induction between the primary and a secondary circuit, the maximum electromotive force round the secondary is MV_0/L, which for a given spark-length is independent of the capacity of the condenser. In practice it is advisable, however, to have as much energy in the jars to start with as possible, and better results are got with large jars than with small ones. Using a six-plate Wimshurst machine I got very good results with two "gallon jars;" with a large induction-coil the best results were got with two "pint and a half jars."

The best number of turns to use in the primary coil C

depends upon the size of the leads; if all the circuit were available for this coil one turn would give the largest electromotive force, because though for a given rate of change of the current in the primary the effect on the secondary increases with the number of turns, the rate of change of the current varies inversely as the self-induction of the primary, so that if all the circuit is in the coil C, since an increase in the number of turns will increase the self-induction of the circuit faster than the mutual induction, it will diminish the electromotive force round the secondary. In practice, however, it is not possible to have the whole of the wire connecting the coatings of the jar in the coil C; and in this case an increase in the number of turns may increase the mutual induction more than the self-induction, and so be advantageous. The best result will be obtained when the self-induction in the coil C is equal to that of the remainder of the circuit. It is very easy to find by actual trial whether the addition of an extra turn of wire is beneficial or the reverse. The brightness of the discharge depends upon the time of the electrical oscillations as well as upon the magnitude of the electromotive force. Thus, in an experiment to be described later, the brilliancy of the discharge was increased by putting self-induction in the leads which, though it diminished the intensity of the electromotive force, increased the time-constant of the system. When the discharge-tube was square and the coil C had also to be square, it was found most convenient to make it of glass tubing bent into the required form and filled with mercury. When, however, the discharge was required in a bulb, the primary coil was made of thick gutta-percha-covered copper wire wound round a beaker just large enough to receive the exhausted bulb. There is sometimes considerable difficulty in getting the first discharge to pass through the bulb, though when it has once been started other discharges follow with much less difficulty. The same effect occurs with ordinary sparks. It seems to be due to the splitting up of the molecules by the first discharge; some of the atoms are left uncombined and so ready to conduct the discharge, or else when they recombine they form compounds of smaller electric strength than the original gas. When the discharge was loath to start, I found the most effectual way of inducing it to do so was to pull the terminals of the Wimshurst far apart and then, after the jars had got fully charged, to push the terminals suddenly together. In this way a long spark is obtained, which, if the pressure of the gas is such that any discharge is possible, with the means at our disposal will generally start the discharge.

Appearance of the Discharge.

Let us suppose that we have either a square tube placed outside a square primary or a bulb placed inside a circular coil of wire, and that we gradually exhaust the discharge-tube, the jars sparking all the time. At first nothing at all is to be seen in the secondary, but when the exhaustion has proceeded until the pressure has fallen to a millimetre or thereabouts, a thin thread of reddish light is seen to go round the tube situated near to but not touching the side of the tube turned towards the primary. As the exhaustion proceeds still further, the brightness of this thread rapidly increases, as well as its thickness; it also changes its colour, losing its red tinge and becoming white. On continuing the exhaustion the luminosity attains a maximum, and the discharge passes as an exceedingly bright and well-defined ring. On continuing the exhaustion, the luminosity begins to diminish until, when an exceedingly good vacuum is reached, no discharge at all passes. The pressure at which the luminosity is a maximum is very much less than that at which the electric strength of the gas is a minimum in a tube provided with electrodes and comparable in size to the bulb. The pressure at which the discharge stops is exceedingly low, and it requires long continued pumping to reach this stage. We see from these results that the difficulty which is experienced in getting the discharge to pass through an ordinary vacuum-tube when the pressure is very low is not altogether due to the difficulty of getting the electricity from the electrodes into the gas, but that it also occurs in tubes without electrodes, though in this case the critical pressure is very much lower than when there are electrodes. In other words, we see that as the state of the bulb approaches that of a perfect vacuum its insulating power becomes stronger and stronger. This result is confirmed by several other experiments of a different kind which will be described later.

The discharge presents a perfectly continuous appearance, with no sign of striation, of which I have never observed any trace on any of these discharges, though I must have observed many thousands of them under widely different conditions.

Action of a Magnet on the Discharge.

The discharges which take place in these tubes and bulbs are produced by periodic currents, so that the discharges themselves are periodic, and the luminosity is produced by currents passing in opposite directions. As this is the case,

it seemed possible that the uniformity of the luminosity seen in the discharge was due to the superposition of two stratified discharges in opposite directions, the places of maximum luminosity in the one fitting into those of minimum luminosity in the other. Since these discharges are in opposite directions, they will be pushed opposite ways when a magnetic force acts at right angles to them, the discharges in opposite directions can thus be separated by the application of a magnetic force and examined separately. In the experiment which was tried with this object, a square tube was used placed outside the primary, the tube at one or two places being blown out into a bulb so as to allow of the wider separation of the constituent discharges. When one of these bulbs was placed in a magnetic field where the force was at right angles to the discharge, the luminous discharge through the bulb was divided into two portions which were driven to opposite sides of the bulb ; each of these portions was of uniform luminosity and exhibited no trace of striation. It was noticed, however, in making this experiment that the discharge seemed to have much greater difficulty in passing through the tube when the electromagnet was on than when it was off. This observation was followed up by several other experiments, and it was found that the discharge is retarded in a most remarkable way by a magnetic force acting at right angles to the line of discharge. This effect is most strikingly shown when the discharge passes as a ring through a spherical bulb. If such a bulb is placed near a strong electromagnet, it is easy to adjust the length of spark so that when the magnet is off a brilliant discharge passes through the bulb, while when the magnet is on no discharge at all can be detected. The action is very striking, and the explanation of it which seems to fit in best with the phenomena I have observed is that the discharge through the rarefied gas does not rise to its full intensity suddenly, but as it were feels its way. The gas first breaks down along the line where the electromotive intensity is a maximum, and a small discharge takes place along this line. This discharge produces a supply of dissociated molecules along which subsequent discharges can pass with greater ease. Thus under the action of these electric forces the gas is in a state of unstable equilibrium, since as soon as any small discharge passes through it the gas becomes electrically weaker and less able to resist subsequent discharges. When the gas is in a magnetic field, the magnetic force acting on the discharge produces a mechanical force which displaces the molecules taking part in the discharge from the line of maximum electric intensity, and thus subsequent discharges

do not find it any easier to pass along this line in consequence of the passage of the previous one. There will not, therefore, be the same instability in this case as in the one where no magnetic force acted upon the gas. A confirmation of this view is, I think, afforded by the appearance presented by the discharge when the intensity of the magnetic field is reduced, so that the discharge just, but only just, passes when the magnetic field is on. In this case the discharge, instead of passing as a steady fixed ring, flickers about the tube in a very undecided way.

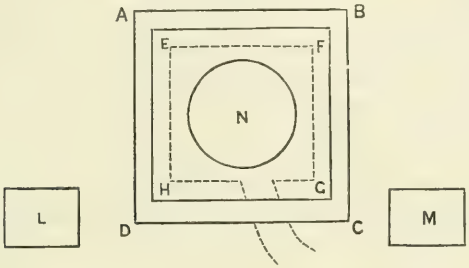
If the strength of the magnetic field is reduced still further, so that the discharge passes with some ease, the bright ring which, when no magnetic force is acting, is in one plane, is changed into a luminous band situated between two planes which intersect along a diameter of the bulb at right angles to the magnetic force. These planes are inclined at a considerable angle, one being above and the other below the plane of the undisturbed ring. This displacement of the ring by the magnetic force shows that it consists of currents circulating tangentially round the ring.

This action of a magnet on a discharge flowing at right angles to its lines of force is not, however, the only remarkable effect produced by a magnet on the discharge. When the lines of magnetic force are along the line of discharge, the action of the magnet is to facilitate the discharge and not to retard it as in the former case. The first indication of this was observed when the jars were connected, as in (*a*) in fig. 1. The earth-connexion being removed, in this case there is a glow from the glass into the bulb, due to the redistribution of the electricity induced on the glass by the primary when it is at a high potential before the spark passes. If the primary is connected to earth by a circuit with an air-break in it, the intensity of the glow may be altered at will by adjusting the length of the air-break; when the air-space is very small there is no glow; when it is long the glow is bright. The bulb in which the discharge was to take place was placed on a piece of ebonite over the pole of an electromagnet, and the air-space in the earth-connexion of the primary was adjusted so that when the magnet was off no glow was observed in the tube. When the magnet was on, however, a glow radiating in the direction of the lines of magnetic force was produced, which lasted as long as the magnet was on, and died away rapidly, but not instantaneously, when the magnet was taken off. In this case the discharge seems to be much easier along the lines of magnetic force.

The following experiment shows that this effect is not

confined to the glow-discharge, but is also operative when the discharge passes entirely through the gas. A square tube ABCD (fig. 6) is placed outside the primary EFGH, the lower part of the discharge-tube CD being situated between the poles L M of an electromagnet. By altering the length of spark of the Wimshurst machine, the electromotive intensity

Fig. 6.



acting on the secondary can be so adjusted that no discharge passes round the tube ABCD when the magnet is off, whilst a bright discharge occurs as long as the magnet is on. The two effects of the magnet on the discharge, viz. the stoppage of the discharge across the lines of magnetic force, and its acceleration along them, may be prettily illustrated by placing in this experiment an exhausted bulb N inside the primary; then the spark-length can be adjusted so that when the magnet is off the discharge passes in the bulb, and not in the square tube, while when the magnet is on the discharge passes in the square tube, and not in the bulb.

The experiments on the effect of the magnetic field on the discharge were tried with air, carbonic acid, and oxygen, but I could not detect any difference in the behaviour of the gases.

The explanation of the longitudinal effect of magnetic force seems more obscure than that of the transverse effect; it is possible, however, that both may be due to the same cause, for if the feeble discharge which we suppose precedes the main discharge branches away at all from the line of main discharge, the action of the magnetic force when it is along the discharge will tend to bring these branches into the main line of discharge; and thus there will be a greater supply of dissociated molecules along the main line of discharge, and therefore an easier path for the subsequent discharges when the magnetic force is acting than when it is absent.

It is perhaps not necessary to assume that the mechanical action of the magnetic force is on a small discharge preceding

the main one; the action of the magnetic force on the chain of polarized molecules which are formed before the discharge passes might produce an effect equivalent to that which we have supposed was produced on an actual discharge.

The chain of polarized molecules would be affected in the following way:—The magnetic field due to the electromagnet consists of tubes of electrostatic induction moving about: these tubes, as well as the direction in which they are moving, are at right angles to the lines of magnetic force. The short tubes of electrostatic induction which join the atoms in the molecules of the gas will, under the influence of the electric forces, set themselves parallel to the direction of the electromotive intensity at each point.

Thus, when the magnetic force is at right angles to the line of discharge, tubes of electrostatic induction parallel to those in the molecules will be moving about in the field; and since parallel tubes exert attraction and repulsion on each other, the molecular tubes will be knocked about and their efforts to form closed chains made much more difficult by the action of the magnet. On the other hand, when the lines of magnetic force are parallel to the discharge, the moving tubes are at right angles to those in the molecules, and will not disturb them in the attempt to form chains along the line of magnetic force, they will in fact assist them in doing so by preventing all attempts in directions across the lines of force.

Prof. G. F. Fitzgerald has suggested to me in conversation that this action of a magnet on the discharge might be the cause of the "streamers" which are observed in the aurora; the rare air being electrically weaker along the lines of magnetic force than at right angles to them will cause the discharge in the direction of those lines to be the brightest.

Discharge through different Gases.

I have examined the discharge through air, carbonic acid, hydrogen, oxygen, coal-gas, and acetylene. As I have already mentioned, at the highest pressures at which the discharge passes through air, the discharge is reddish, and gets brighter and whiter at lower pressures. If the discharge is examined through a spectroscope, the lines in the spectrum coincide with those obtained by sparking through air in the ordinary way with a jar in the circuit. The relative brightness of the lines in the spectrum of the discharge without electrodes varies very much with the pressure of the gas and the length of spark in the jar circuit. With a long spark in this circuit, and the pressure such as to give a bright white

discharge, the spectrum is very much like that of the ordinary jar-discharge in air. When, however, the pressure is so low that the discharge passes with difficulty, a few lines in the spectrum shine out very brightly, whilst others become faint, so faint indeed sometimes that if the air-spectrum were not thrown into the field of view of the spectroscope at the same time, they might pass unnoticed. Three lines which are very persistent, the first a citron-green, the second a more refrangible green, and the third a blue, I am inclined to think must be due to mercury vapour from the pump.

I am indebted to Prof. Liveing for the loan of a very fine direct-vision spectroscope, and to him and Mr. Robinson, of the Cambridge Chemical Laboratory, for valuable advice in the attempts which I made to photograph the spectra of some phosphorescent glows mentioned below.

I should like to call attention to the advantages for spectroscopic purposes which attend this method of producing the discharge; it is easily done either by an ordinary electrical machine or an induction-coil. An intensely bright discharge is got, and there is no danger of complication arising from the spectrum of the gas getting mixed with that of the electrodes.

Discharge in Oxygen.

By far the most remarkable appearance is presented when the discharge passes through oxygen, for in this gas the bright discharge is succeeded by a phosphorescent glow which lasts for a considerable time; indeed, with a strong discharge it may remain visible for more than a minute. When the discharges succeed one another pretty rapidly, the phosphorescence is so strong that it hides the successive bright discharges, and the tube seems permanently full of a bright yellow fog. We can thus by the use of this gas convert the intermittent light given by the bright discharge into a continuous one.

Perhaps the most striking way of showing this phosphorescence is to use a long tube, about a metre long and 6 or 7 centimetres in diameter, with a bulb blown in the middle, the primary coil being twisted round this bulb. Then, when the sparks pass between the jars, a bright ring-discharge passes through the bulb, from which, as if shot out from the ring, the phosphorescent glow travels in both directions along the tube, moving slowly enough for its motion to be followed by the eye. It cannot, therefore, be produced by the direct action of the light from the spark on the gas in the tube, for

if it were, the glow would travel with the velocity of light. It is necessary to mention this point, for the light from these discharges has great powers of producing phosphorescence.

The glow seems to consist of gas which has been in the path of the discharge, and whose molecules have been split up by it and projected from the line of discharge. This gas which, when projected, is in a peculiar state, by a process of chemical combination gradually returns to its original condition, and it is while it is in this state of transition from its new condition to the old that it phosphoresces. If this is the case we should expect that the period of phosphorescence would be shortened by raising the temperature. On trying the experiment I found that this took place to a very marked extent. A discharge-bulb filled with oxygen at a low pressure was placed over a Bunsen burner; before the bulb got hot each bright discharge was succeeded by a bright afterglow, but as the bulb got hotter and hotter the glow became fainter and fainter, and at last ceased to be visible, though the bright ring was still produced at each discharge of the jar. When the Bunsen was taken away and the bulb allowed to cool, the glow reappeared.

The spectrum of the afterglow is a continuous spectrum, in which I could not detect the superposition of any bright lines. The only gas besides oxygen in which I have been able to detect any afterglow is air, though in this case the range of pressure within which it is exhibited is exceedingly small; indeed it is often by no means an easy matter to get a bulb filled with air into the state in which it shows the glow. The spectrum of the air-glow showed bright lines; I thought myself that I could see a very faint continuous spectrum as well. Some friends, however, who were kind enough to examine the spectrum, though they could see the bright lines clearly enough, were of opinion that there was nothing else visible. I endeavoured to photograph it, but without success, so that the existence of a continuous spectrum for this glow must be considered doubtful.

When the discharge passes through acetylene, the first two or three discharges are a bright apple-green, the subsequent ones, however, are white, and as the green discharge does not reappear, we must conclude that the acetylene is decomposed by the discharge.

[To be continued.]

XLII. *Notes on Allotropic Silver.* *By* M. Carey Lea*.

RELATIONS of the Yellow to the Blue Forms.—The gold and copper-coloured forms on the one hand, and the blue, bluish-green, and steel-grey on the other hand, stand in close relations to each other. In previous papers there has been described a crystalline state intermediate between these active forms and ordinary silver, which intermediate condition, whilst retaining the bright yellow colour of the active form, is nearly as indifferent to reagents as ordinary silver. Into this intermediate state both the yellow and blue forms are capable of passing, and apparently the intermediate states of both kinds of allotropic silver are identical: *the intermediate form of blue silver is yellow.* Thus, when lumps of blue silver are heated in a test-tube to about 180° C., they assume a gold colour and lustre. The same change takes place at the same temperature when films of blue silver are placed in a hot-air bath.

But relations much closer than these exist. Blue silver can be converted into yellow at ordinary temperatures and consequently with retention of its active properties. This is accomplished through the agency of sulphuric acid. When a solution of silver is obtained by the action of sodium hydroxide and dextrine on silver nitrate†, it appears to contain the blue variety; for if allowed to precipitate spontaneously by long standing, or if precipitated by acetic acid, dilute nitric acid, or by many neutral substances, it gives a form of silver which is dark red whilst moist and dries with a blue surface-colour. (It is always a little difficult to characterize these substances by their colours, since the surface-colour which they show when dry, either in mass or in films, is mostly complementary to their colour when wet. As the surface-colour is much the more characteristic, I have adopted the course of naming them by that.)

The behaviour of the red solution obtained by soda and dextrine with dilute sulphuric acid is very interesting and

* From an advance proof communicated by the Author.

† Forty grams each of sodium hydroxide and of yellow or brown dextrine (not white) are dissolved in two litres of water, and twetny-eight grams of silver nitrate in solution are added in small quantities at a time, with frequent stirring, so that several hours shall elapse before the last portion is added. The solution is always slightly turbid when viewed by reflected light, by which it shows a beautiful deep green colour. By transmitted light it is deep red, and, when diluted, absolutely transparent. By diminishing the proportion of silver nitrate to one half, a solution nearly or quite clear by reflected as well as by transmitted light is obtained.

instructive. When 100 cubic centim. of solution are poured into 100 cubic. centim. of water to which 3 cubic centim. of sulphuric acid have been previously added, a dark red precipitate falls, which, when dry, especially in films, is blue. The mixed liquid from which the precipitate is formed is acid. Increasing the proportion of acid to 4, 5, and 6 cubic centim. successively, the substance obtained has a green surface-colour, becoming more yellowish green in proportion as the acid is increased in quantity. With $7\frac{1}{2}$ cubic centim. the substance no longer dries green, but yellow. Increased proportions of acid produce substances drying with a coppery shade.

It will be seen that from a single solution, and using one substance only as a precipitant, we can obtain the whole range of different forms of allotropic silver by simply varying the proportions of the precipitant.

That these forms of silver should subsist in the presence of sulphuric acid in excess is remarkable. For the most part the presence of this acid tends to quickly convert allotropic to ordinary silver. For example, bright yellow allotropic silver obtained with ferrous tartrate was washed on a filter with water containing $\frac{1}{500}$ its volume of sulphuric acid : in two or three hours the entire mass was converted into grey ordinary silver.

It is observable that the substances precipitated with the least acid have a very splendid lustre, and that this lustre diminishes steadily as the proportion of acid is increased. Up to 6 to 100 cubic centim. the effect is hardly noticeable, after that it becomes more marked.

But we can also obtain the converse of this reaction. Just as the solution which naturally would yield the blue product can be made to yield the yellow by the presence of excess of strong acid, so the solution which normally yields the yellow substance may be made to produce blue (or rather green) silver by adding alkali. Thus a mixture of dilute solutions of ferrous sulphate and of Rochelle salt added to mixed solutions of silver nitrate and of Rochelle salt results in the formation of gold-coloured silver. But if we add a little sodium hydroxide, either to the iron solution or the silver mixture, we shall get a bluish-green product, whose properties show that it belongs to the blue class and not to the yellow. Even if a solution of the hydroxide is added immediately after the iron solution has been poured into the silver, the result is the same.

There is, therefore, a well-marked tendency of acids to give rise to the formation of the yellow product and of alkalies to the blue. But this is a tendency only. Both substances can be produced from neutral solutions, and slight changes are

sufficient to alter the product formed. Thus, ferrous tartrate in dilute solution acting on silver tartrate gives rise to the formation of the gold-coloured substance, but when citrates are substituted the blue substance is obtained.

Production of Allotropic Silver by Inorganic Substances.—For reasons which will be mentioned presently the reduction of silver must take place gradually to produce the allotropic form, and for a time it seemed an invariable condition that an organic substance of some sort should be present. This, however, proves not to be essential. In a paper presented to the American Academy, and kindly read for me by Prof. Remsen at the meeting in April last, I alluded briefly to having found a reaction depending upon inorganic agents only. It is as follows:—Sodium hypophosphite added to silver nitrate does not effect reduction; but when hypophosphorous acid is set free by the addition of phosphoric acid, a red coloration appears, indicating the presence of allotropic silver. The coloration is transitory, no doubt because of the strong tendency of free mineral acids to convert allotropic to normal silver; but red and blue stains form on the sides of the vessel.

Phosphorous acid gives similar results, though perhaps less well marked.

Action of Light on Blue Silver.—This action differs with different varieties: it was more especially examined with the form that is obtained from the soda-dextrine silver solution already described, by pouring the solution into an equal bulk of water to which sulphuric acid had been added in the proportion of 4 cubic centim. to each 100 cubic centim. of water. This form was selected because it is easy to obtain with great constancy of result, and because it is one of the forms of blue silver most sensitive to light.

Exposed to light this substance first becomes more distinctly blue, losing a slight greenish shade. With continued exposure it passes to a yellow-brown shade, and finally to a perfectly pure golden yellow of great brilliancy and lustre. This last is the intermediate or crystalline form.

The action of light on this form of silver is remarkable in this respect, that its first effect is to *increase* the sensitiveness to reagents.

This result was so unexpected, and *à priori* so improbable, that it was subjected to the most careful verification before being accepted. The action is very easily shown by exposing a film of the substance to light, covering part of the surface with an opaque screen. After twenty or thirty minutes of exposure to strong summer sunshine the film may be plunged

into a 1-per-cent. solution of potassium ferridcyanide, when the part exposed colours much sooner and more strongly than that which was covered. The effect is shown still better by placing the film in a frame, covering part with paper rendered absolutely opaque by coating it with thick tin-foil, part with translucent paper (thick white writing-paper or very thin brown paper), and leaving part wholly exposed. After four or five hours' action of strong summer sunshine, the film is to be treated with weak ferridcyanide. The part wholly exposed having passed into the gold-coloured crystalline condition (if the exposure has been sufficient) is wholly unacted upon ; the part covered by the translucent paper is rapidly attacked, that wholly protected is attacked slowly. So that the portion moderately acted on by light has very markedly increased in sensitiveness thereby.

It follows that upon this form of silver *light has a reversing action*, first exalting its sensitiveness, then completely destroying it.

It is impossible to overlook the analogy which exists between this action of light and that which light exerts on silver bromide. The latter substance, though incomparably more sensitive to light, is subject to the same reversing action ; first gaining in sensitiveness to reducing agents, and then, by continued exposure, becoming less sensitive than originally, a change commonly known as solarization.

Causes determining whether, in the reduction of Silver, the Allotropic or the Normal form shall be produced.—I have examined the phenomena connected with the reduction of silver under a great variety of conditions. These for the most part do not deserve particular mention, but seem to lead up to this generalization : that the reduction of silver may be direct or indirect ; direct when it passes from the condition of the normal salt or oxide to that of the metal, indirect when the change is first to suboxide or to a corresponding subsalt. So far as my observation has gone, when the reduction is *direct* the reduced silver always appears in its ordinary form ; but when the reduction is *indirect* the silver presents itself in one of its allotropic states.

The following reactions support this view.

Three of the principal modes of formation of allotropic silver are:—(1) Reduction of silver citrate or tartrate by ferrous citrate or tartrate ; (2) acting on silver nitrate or oxide by dextrine and fixed alkaline hydroxide ; (3) acting on silver nitrate or carbonate by tannin and fixed alkaline carbonate. Now if, in either of these three cases, we interrupt the action before it is complete by adding an excess of dilute

hydrochloric acid, we shall obtain a dark chestnut-brown or sometimes purple-brown substance, which on examination proves to be a mixture of silver subchloride and protochloride. When, after complete removal of the excess of hydrochloric acid by thorough washing or, better, by boiling with distilled water, the substance is treated with cold dilute nitric acid, that portion of the subchloride which is not combined with the normal chloride is broken up, and there remains protochloride of a very rich and intense rose-colour *.

The production of silver subchloride in all these cases would seem to indicate that the reduction when the acid was added was incomplete ; and that in case (1) a subsalt, and in cases (2) and (3) a suboxide was first formed as an intermediate step before complete reduction. Either of these substances would of course give rise to the formation of subchloride when treated with hydrochloric acid. It is important to observe that this result is to be obtained only by interrupting the reaction before it is complete. When, for example, allotropic silver in solution is produced by the action of sodic hydroxide and dextrine, and after complete reduction hydrochloric acid is added, the liquid becomes filled with grey normal silver which presently collects to a cake. When this cake is well washed and boiled with water and then treated with dilute nitric acid, solution takes place : a trace of protochloride is left behind. It has been mentioned elsewhere that hydrochloric acid, though without action on ordinary silver, is capable of forming a variable quantity of protochloride when placed in contact with allotropic silver.

I have not met with any exception to this general principle, that when a reaction leading to the formation of allotropic silver is interrupted by the addition of hydrochloric acid, subchloride is abundantly formed as one of the products.

In all such cases the reduction is evidently indirect. The silver does not lose at once the whole of its oxygen, but apparently passes through an intermediate form, probably Ag_4O, the reduction of which tends to the formation of allotropic silver.

These facts lead directly up to the question, Does silver exist in its subsalts in the allotropic form? There are some facts that would support this view, especially the very rich and varied coloration of the subsalts corresponding to the

* This is a very beautiful reaction and deserves more particular mention than can be given here. It is perhaps the best means for obtaining silver protochloride, for which purpose I have often employed it, both on account of its facility and certainty, and the very beautiful colour of the product.

almost infinite variety of colour of allotropic silver, whilst normal salts of silver when formed with colourless acids are mostly colourless. On the other hand, the greater activity of allotropic silver and its less specific gravity would seem to indicate a simpler molecular constitution than that of normal silver.

XLIII. *Some Applications of Physics and Mathematics to Geology.* *By* C. CHREE, *M.A., Fellow of King's College, Cambridge.*

[Continued from p. 252.]

PART II. *Some Geological Theories.*

THE belief that the present spheroidal *form* of the earth necessarily betokens a previous liquid, or at least plastic, condition seems amongst Geologists almost as universal as the belief that the earth but for the development of rotation must have been a spherical body. Whether this latter conclusion has any satisfactory basis apart from philosophical speculations, it is not my present object to inquire. But supposing, for the sake of argument, that the natural form of the earth as undisturbed by rotation is spherical, the conclusion that it ever was in a liquid or even in a plastic state throughout is, according to the preceding results, not established by its present spheroidal form. Yet even in such a standard work as Geikie's 'Text-book of Geology,' after reading the discussion on p. 12 and the footnote attached, I fail to detect a trace of the idea that the polar flattening might be called forth by rotation in a truly solid body.

Various geological writers, it is true, speak of a solid earth as capable of changing its form, but they seem in reality to regard the change as due to rupture or to the development of a plastic condition. This appears, for instance, to be the view actually held by Mr. Herbert Spencer in a short paper* entitled "The Form of the Earth no proof of Original Fluidity." This paper has been referred to with a somewhat inaccurate conception of its value and results by two recent geological writers, so it claims some notice at our hands. The first of the two writers referred to, Mr. W. B. Taylor†, says :—"It is now nearly forty years since Herbert Spencer, with a juster physical insight [than Sir W. Thomson and Professor Tait], contended and satisfactorily showed that a solid earth (of any shape) would assume the oblate spheroidal

* Phil. Mag. [3] vol. xxx. 1847, pp. 194–196.

† American Journal of Science, vol. xxx. 1885, pp. 258, 259.

form due to its rate of rotation, as certainly and promptly as if it were liquid." The other writer, Mr. A. Blytt*, amongst other references to the paper says, "I believe that Spencer is the first who expressed the opinion that even a solid earth can change its form."

Mr. Spencer, after some statements as to the relative strength and agility of large and small animals, such as elephants and fleas, formulates the general result that the strength—called also "resistance to fracture"—of a solid structure varies as the square of its linear dimensions, while the "agencies antagonistic to cohesive attraction," *i.e.* gravitational and "centrifugal" forces, &c., vary as the cube. Excepting a statement that this is obviously true of simple longitudinal and torsional stress, the following is the sole proof of his very general law supplied by Mr. Spencer :—"The strength of a bar of iron, timber, or other material subjected to the transverse strain varies as BD^2/L ; B being the breadth, D the depth, and L the length. Suppose the size of this bar to be changed, whilst the ratios of its dimensions continue the same ; then . . . the strength will vary as D^2 . . ." (p. 195). The following is the conclusion drawn by Mr. Spencer :—"Viewed by the light of this principle, the fact that the earth is an oblate spheroid does not seem to afford any support to the hypothesis of original fluidity as commonly understood. We must consider that, in respect of its obedience to the geo-dynamic laws, the earth is fluid now and must always remain so ; for the most tenacious substance with which we are acquainted, when subjected to the same forces that are acting upon the earth's crust, would exceed the limit of self-support determined by the above law, before it attained $\frac{1}{1,000,000,000}$th of the earth's bulk" (p. 196).

Perhaps if one knew what Mr. Spencer means by "the limit of self-support," and what is the exact distinction he draws between "fluidity as commonly understood" and "fluidity in respect of obedience to geo-dynamic laws," one might be in a position to form some estimate of his degree of physical insight ; but so far as I can see all he satisfactorily shows is an extraordinary agility in jumping to conclusions. If his meaning is that deformation must accompany the action of gravitational and centrifugal forces, he might, if Maxwell's view be correct, have added to the denominator of his estimate as many 0's as the printer could spare ; but if it is the rupture of an elastic solid or its transformation into a

* Phil. Mag. May 1889, p. 415. Translated from *Nyt Magazin for Naturvidenskaberne*, Bd. xxxi. 1889.

plastic state to which he refers, as seems almost certain from the context, he must have formed an extremely low estimate of what strains a solid can stand.

In the same passage Mr. Blytt refers to Mr. Peirce*, Sir J. W. Dawson†, and Professor J. E. Todd‡ as holding that a solid earth will alter its shape if the rate of rotation vary. The views of Mr. Peirce I have not seen, but the other two writers mentioned regard the solid earth itself as changing shape only by means of a succession of what we may term catastrophes. Their views seem identical with those which Mr. Blytt's translator ascribes to him in the following words: —"The sea adjusts itself in accordance with the smallest change in the length of the day . . . . But the solid earth offers resistance to change of form, and begins to give way only when the tension reaches a certain amount" (p. 418). Mr. Blytt makes several distinct references to the subject, and his remarks are not perhaps always strictly consistent. This, however, is hardly to be wondered at since he gives as the result of his investigations:—"As has been stated, there prevails . . . a disagreement as to how far the earth will change its form, in case the centrifugal force varies. Thomson is most inclined to believe that it will not; Darwin is of opinion that it will. And among other physicists whom I have consulted a similar divergence prevails upon this point. One thinks that a lengthening of the day even by several hours will be incapable of altering the form of the solid earth; another believes that the solid earth will probably change its form just as easily as the sea" (p. 421).

If Mr. Blytt should ever have further occasion to consult physicists on this or any allied point, he would find an exact definition of such terms as *solid* a certain amount of protection from *à priori* speculations. Mr. Blytt's own principal view seems due in part to an erroneous interpretation of Tresca's experiments on the flow of metals under pressure. They do not in reality justify his statement "By reason of the enormous pressure which prevails in the interior of the earth, it must be supposed that masses from a certain depth are more or less in a plastic state" (p. 417). It was in fact pointed out some years ago by the Rev. Osmond Fisher§ that the existence of an orifice from which the metal can flow constitutes a complete difference between the conditions of

* Proc. Amer. Acad. Arts and Science, vol. viii. 1873, p. 106.
† 'Story of the Earth and Man,' ninth edition, pp. 291, 292.
‡ American Naturalist, vol. xvii. 1883, pp. 15–26, specially pp. 18, 19.
§ 'Physics of the Earth's Crust,' 1st edition, 1881, footnote p. 120.

Tresca's experiments and the state of a body subjected to nearly uniform pressure all round.

Mr. Blytt apparently does not stand alone in believing Sir W. Thomson to hold that the solid earth is incapable of altering its form as the rotation alters, and that it possesses the same eccentricity as when it solidified. Professor Darwin in 'Nature,' vol. xxxiv. (1886), pp. 420–3, seems also to put this interpretation upon a passage he quotes from § 830 of Thomson and Tait's 'Natural Philosophy.' Supposing this interpretation correct, Professor Darwin's opinion that Sir W. Thomson does not allow "a sufficient margin for uncertainties" expresses only a part of the objections I should entertain. I find it difficult, however, to believe that Sir W. Thomson, who elsewhere gives data for the eccentricity produced by rotation in solid spheres of steel, can actually suppose no change at all in the eccentricity to follow an alteration in the angular velocity. Still it must be confessed that though the passage contains the statement, "It must necessarily remain uncertain whether the earth would from time to time adjust itself completely to a figure of equilibrium adapted to the rotation," its most natural interpretation is that given by Professor Darwin. I need hardly say that the conclusion that the earth, however solid, would retain a constant eccentricity while the rate of rotation varied, seems to me directly opposed to the conclusions to which the elastic solid theory leads.

Professor Darwin himself, in his paper in 'Nature,' refers to Tresca's experiments and thinks it probable there would be from time to time a flow of material as the angular velocity altered. One of the "uncertainties" he refers to is the possibility that, in accordance with Dr. Croll's* views, a greater rapidity of denudation in equatorial than in polar regions may have reduced the eccentricity markedly below the value it possessed when the earth solidified. He does not seem, however, to refer to the considerable change of eccentricity that might occur in a solid through mere variation of elastic strain.

As regards the present state of the earth's interior there are, according to Geikie's 'Text-book,' p. 49, only three theories which merit serious consideration, viz.:—

(1) That there is a solid crust and a molten interior.
(2) That with the exception of local vesicular spaces the earth is perfectly solid.
(3) That the earth consists of a solid crust and nucleus with an intervening liquid layer.

* 'Climate and Time' (1885), p. 336.

According to the 'Text-book,' the theory of a *thin* crust containing liquid or viscous matter is exposed to "weighty and indeed insuperable objections," p. 18, and "is now abandoned by most geologists," p. 43.

According to Dr. Croll* the "general opinion among geologists" is that the earth "consists of a fluid interior surrounded by a thick and rigid [really solid] crust."

Professor Prestwich † believes that "the crust rests on a yielding substratum, and that of no great thickness." In fact he advocates the third of the above-mentioned theories, and believes 30 miles to be probably in excess of the crust's thickness. Most writers on the subject appear to have subsidiary theories of their own.

Whether the assurance that the question is beyond the reach of experiment accounts for the multitude of theories and the confidence with which they are proposed, is a question for philosophers not mathematicians to consider, but it seems *à priori* a possible explanation of such a declaration of faith as that of Mr. W. B. Taylor ‡ :—"The liquidity of our globe, and the relative thinness of its encrusted envelope,—as attested by all legitimate *geological* induction,—will be assumed without misgiving or hesitancy ; and the supposed mathematical arguments for its solidity ignored as essentially fallacious and wholly inconclusive."

Of course, if the geological evidence were conclusive, it would be mere waste of time further to consider the matter, but the evidence that satisfies Mr. Taylor does not seem to carry conviction to all geologists even in America. Mr. G. F. Becker §, for instance, who appears to have some practical experience, says :—"For a considerable number of years I have constantly had the theory of the earth's solidity in mind while making field observations on upheaval and subsidence, with the result that to my thinking, the phenomena are capable of much more satisfactory explanation on a solid globe than on an encrusted fluid one."

It may thus be not wholly unprofitable to glance briefly at some of the arguments which some of the advocates of the several theories base on their ideas of the properties of solid bodies.

Mr. Taylor's object is to get an equatorial circumference some 10 per cent. in excess of its present value, so as to account for the lateral compression at the surface observed in

* 'Climate and Time,' p. 395.
† 'Geology,' vol. ii. p. 540.
‡ American Journal of Science, vol. xxx. (1885), p. 250.
§ American Journal of Science, vol. xxxix. (1890), pp. 351, 352.

mountain-chains. Thus, following Professor Darwin*, he supposes the earth to have once possessed a much greater angular velocity than at present, and speaks of a "consistent crust (of some few miles thickness)" as having formed "when the rotation of our planet was at four times its present rate" (*l. c.* p. 257). The equatorial radius would then have been, he says, some 4359 miles, and the polar some 3291. The change of shape, as the rotation fell off, would account, he thinks, for observed phenomena. He considers his conclusions opposed by Sir W. Thomson's theory that the earth solidified throughout and retains at least approximately its original eccentricity. It is on this point that he refers to the data supplied by Mr. Herbert Spencer's "juster physical insight;" and he adds, apparently as his own contribution to the argument,—"The supposition that a granite mountain or equatorial protuberance 400 miles high or 100 miles high could for a moment support itself, would hardly be entertained by a practical engineer;" and in a footnote, "The limiting modulus of height of a granite pyramid (equalling one side of its square base) is somewhat less than eleven miles" (*l. c.* p. 258). I am quite ready to agree with Mr. Taylor that if solidification occurred under the conditions he supposes the eccentricity must have altered enormously and that in a non-elastic way, and I hardly suppose that Sir W. Thomson would oppose this view. No one, however, so far as I know, has propounded the theory of an elastic solid spheroidal earth of eccentricity ·65 rotating completely in six hours, so that the investigation of the strains and stresses required by such a theory is unnecessary. I can quite imagine that on any probable theory of density the magnitude of the strains is hardly likely to be consistent with the application of the mathematical theory of elasticity. The force of Mr. Taylor's remarks as to the pyramid I, however, fail to see. Such an isolated mass exists under totally different conditions from any portion of a solid sphere or spheroid, and one might as well argue as to the impossibility of a liquid interior from the fact that an isolated liquid column 100 miles high has not yet been observed on the earth's surface. If Mr. Taylor were, however, to calculate the strains and stresses in such a thin shell as he supposes, of material showing anything resembling the structure of ordinary rock, with a rate of rotation such as he mentions, I very much doubt whether he would find it in an essentially better position than his imaginary pyramid.

After this criticism Mr. Taylor considers the question of the probable degree of rigidity of our planet quite irrelevant, but

* Phil. Trans. (1879), p. 532.

the "temptation is strong to waste upon it a collateral glance" (*l. c.* p. 259). Accordingly he crushes Sir W. Thomson's argument* from the tides by the remark—"That a siliceous crust of 20 miles average thickness, and an overlying aqueous ocean of three miles average depth, should have (as required by the argument) so equal a coefficient of mobility, that sea and land could thus together 'rise and fall,' might well be pronounced incredible" (*l. c.* p. 260).

He regards Sir W. Thomson as very seriously damaging his own argument by the admission that tides comparable in magnitude with those observed would occur even in a solid earth of steel. It does not seem to have occurred to him that the existence of a difference between the motions of the land and water may constitute an argument for solidity†.

Mr. Taylor admits one difficulty in his theory, viz. the nature and local characteristics of the plications actually observed; and remarks:—"While the *force* at the command of the rotating planet is abundantly sufficient . . . evidently some supplementary considerations are requisite to give the observed *direction* to this force," . . . "The mere mechanical difficulty, however, of transmitting stresses through comparatively undisturbed areas of hundreds of miles of a flexible, friable, and practically plastic crust—with a large coefficient of viscous friction beneath—is not so formidable as might at first appear. It must be borne in mind that the pressures derived from an action so slow as from century to century to be scarcely sensible, are of an order of very great intensity, but of very small quantity" (*l. c.* p. 265). Mr. Taylor also infers from "various considerations" that "in all ages mountain building has been at a maximum; that is, the uplifted heights have been the greatest which the average thickness of the crust at the time was capable of supporting; so that the former has been a constant function of the latter, the ratio being probably not far from one-fifth" (*l. c.* p. 265). Mr. Taylor does not state that this law of the uplifted heights is true of all lands as well as of all time, but the possibility that such may be the case is rather alarming. He enters in fact into no unnecessary details as to how he reached his conclusions, so that all one can say is that measured by his own standard he is certainly not inferior in physical insight even to Mr. Herbert Spencer. Perhaps when he comes to deal with the "supplementary considerations" he may supply sufficient data for the mathematician to follow him.

Professor Prestwich, in his 'Geology,' vol. ii., regards the

* Natural Philosophy, vol. i. part ii. § 833.

† See his remarks, *l. c.* p. 260 and footnote.

"present very great rigidity of the earth" as proved by mathematical and physical investigations, but complains of a " want of elasticity " in the methods of the mathematicians (p. 538). According to him, " The hypothesis most compatible with the geological phenomena is that of a central solid nucleus with a molten yielding envelope—not fluid, but viscid or plastic; nor is it necessary that this magma should be of any great thickness ; but a thin crust is, it seems to me, an essential condition" (p. 543). Professor Prestwich adduces in support of his views various arguments from geological phenomena which seem of much weight. He has also various arguments of a more or less physical character, but they seem to take a good deal for granted. Thus, on p. 540, referring to plications in the surface rocks, he says, " if the earth were solid throughout, the tangential pressure would result not in distorting or crumpling, but in crushing and breaking. As a rule no such results are to be seen, and the strata have . . . yielded, as only a free surface-plate could, to the deformation caused by lateral pressure . . . a yielding bed, on which the crust could move as a separate body, was necessary." It seems to me that as the phenomena of rupture are as yet very imperfectly ascertained, except perhaps for a few simple standard conditions, Professor Prestwich has very little to go on but *à priori* ideas. I fail to see, for instance, why pressures at or near the surface of a solid sphere should necessarily produce fracture and not flow. Also it seems improbable that there would be a sharp line of demarcation so as to enable a crust—which seems clearly to mean a solid superficial layer—to move as a separate body on a " yielding bed." Would not this imply a liquid substratum with no appreciable viscosity? And supposing there were a substratum of this kind, is there any sufficient experimental evidence that a solid crust of even a few miles thickness would on the falling away of the liquid underneath go into folds instead of being crushed and broken? Further, can plications, to the extent shown, say by the Alps, be reconciled with the retention of contemporaneous solidity? Supposing the earth to be essentially solid throughout, is there any reason why the strain at some miles below the surface should not locally at intervals exceed the elastic limit, with the result for a time of a state of flow or plasticity throughout a volume of greater or less extent? During such an epoch there would exist locally conditions somewhat resembling those which Professor Prestwich believes existent everywhere. It is true that one argument adduced by Professor Prestwich and others against the existence of separate reservoirs of molten material—viz. the similarity in the character of volcanic products

all over the earth—applies equally against such an hypothesis. If, however, volcanic products be supposed to come from several miles below the surface, I see no obvious reason why they should not present similar characteristics everywhere. No conclusive argument can well be based on the differences observed in the sedimentary strata, because the conditions under which such strata are deposited are obviously of a varied character.

In various passages of Professor Prestwich's discussion of the state of the earth one is apt to be puzzled by his falling into the practice, by no means uncommon in geological writings, of employing physical terms with a view to oratory rather than to exposition. For instance, he speaks of contraction "due to the yielding of the weaker lines in the crust, when the tension caused by the excessive strain (and of which the first order of movement is an index) overcomes the resistance, and fractures and doubles up the strata;" and he adds, "Mountain-ranges are in fact the concluding term of the stress which caused the deformation of the crust, and the movements which at those times took place must have been influenced by the greater energy of the strains then at work" (p. 546). It is difficult to see here what is intended to be cause and what effect. In fact, while a number of terms are employed which in mathematics and physics have a fairly definite meaning, I must confess my inability to form an adequate conception of what is meant by the passage as a whole.

Professor Prestwich refers (pp. 543, 544) to the hypothesis of the late Professor E. Roche (in the reference to which a misprint gives the year 1861 for 1881) as supplying something of the kind of earth he wants. Thus an examination of Professor Roche's work* may be of some service.

He supposes the earth to consist of a central nucleus or "bloc," homogeneous but for a possible accumulation of matter of greater density at the centre, and of a superficial layer of lighter material. Of the nucleus, with the possible exception of a small core of heavier matter, he says, "Sa densité calculée, de 7 à 7·5, indique qu'elle est métallique, sans doute formée de fer...." The specific gravity of the heavier matter which may possibly exist at the centre is, he says, "certainement bien inférieur [to 18], probablement 10 ou 12 (argent, plomb)," p. 235. The outer layer or crust he supposes to have a specific gravity about 3, and a thickness of about one sixth the earth's radius. Between the crust and the nucleus there exists, it may be everywhere or only locally,

* *Académie ... de Montpellier, Mémoires de la Section des Sciences*, tome dixième, 1880–84, pp. 221–264.

molten matter such as appears at the surface in volcanic outbursts, but the total volume occupied by this must be small. Professor Roche takes three results as given ; viz. the earth's total mass, the eccentricity of its surface, and the ratio of the principal moments of inertia, the last quantity being deduced from astronomical data. He satisfies all the conditions he recognizes by the aid of the following hypothesis regarding his nucleus :—"Ce bloc a pris sa forme définitive sous l'influence d'une rotation moins rapide qu'elle n'est aujourd'hui, et il a conservé l'aplatissement correspondant, malgré les accroissements successifs de vitesse du système résultants de sa contraction progressive" (p. 232). In other words, he assumes the nucleus to have solidified before the crust and that it retains its shape unaltered. Thus as he regards the angular velocity as *increasing* in consequence of the diminution in the moment of inertia through contraction in cooling, the nucleus possesses a *smaller* eccentricity than the crust. He supposes only a small difference in the length of the day at the dates of the two solidifications, so that the difference between the eccentricities of the nucleus and crust is also small. This, however, in no way justifies his hypothesis that the nucleus retains its form unaltered. If its material possessed the properties of an elastic solid the eccentricity would certainly alter, and to an extent probably quite comparable with the alteration that would have occurred if it had remained fluid. Professor Roche seems in fact to treat his nucleus as possessed of the properties of the wholly imaginary perfectly rigid body. He certainly introduces no equations such as ought to hold over the surface of an elastic solid spheroid. The exact view he adopted as to the properties of solids it is, however, difficult to decide. On his p. 241 a brief statement would imply that he did not regard each elementary layer of a solid sphere as of necessity totally self-supporting ; but on pp. 223, 224, where the discussion is fuller, he says, "Si l'on rejette la complète fluidité de la terre, il n'est plus possible d'attribuer à la compressibilité de ses couches la même influence." . . . "Dans un solide, les tensions latérales sont variables et acquièrent parfois une valeur énorme. C'est ainsi qu'une couche pourrait se soutenir d'elle-même comme une espèce de voûte, sans peser sur celle qui est au-dessous." A solid layer supporting itself like an arch under the conditions of matter near the earth's surface treated as an elastic solid, presents strains far in excess of those which are regarded here as coming within the range of the mathematical theory.

On various grounds it seems to me that the criticism of a want of elasticity, though hardly in the sense intended by

Professor Prestwich, may be strongly urged against Roche's investigations.

Some remarks of M. Roche's, on his pp. 240, 241, throw considerable light on his standpoint and that of many other theorists :—"Les astronomes qui persistent à admettre la fluidité . . . . cherchent à éluder les objections de Hopkins et de Thomson, en attribuant . . . . au liquide central une viscosité assez grande pour que . . . . l'ensemble en arrive à tourner tout d'une pièce . . . . La masse tournante offre une telle rigidité qu'elle est assimilable sous ce rapport à un bloc solidifié, mais admettre cette assimilation revient à dépouiller le milieu interne des propriétés ordinaires des liquides, et à lui en conserver le nom tout en l'identifiant à un corps solide." He proceeds to point out that the mere question of a name is of no account, considering our ignorance of what would be the properties of matter under such pressures and at such a temperature as the theory of fluidity would lead to. His line of argument is not very clear, but there is no hesitation apparent in his conclusion :—"En effet, la pression supportée par les couches centrales, dans la supposition d'une complète fluidité, dépasserait deux millions et demi d'atmosphères. La grandeur même de ce nombre est à elle seule une objection péremptoire à l'hypothèse qui y conduit."

Such a position as this may be all very well for a philosopher who supposes the external world a mere idea, the private property of his own mind and so necessarily obedient to laws which his understanding can fully grasp, or for a scientist who believes the earth created for the special purpose of supplying problems of precisely that amount of difficulty which he personally is able to solve, but from a common-sense point of view it seems utterly irrational. No physicist or geologist has any reason to suppose that there are not numerous problems whose full comprehension requires more extensive knowledge than is possessed by himself or any of his contemporaries.

The necessity for theories has been eloquently urged by Professor Darwin *, who says "A theory is, then, a necessity for the advance of science, and we may regard it as the branch of a living tree, of which facts are the nourishment." Employing this simile, I must confess that the subject treated in this paper resembles, in my opinion, a tree which combines a sad deficiency of sap with a great superfluity of branches. It will, I dare say, be generally admitted that the premature craving

* 'Nature,' vol. xxxiv. (1886) p. 420, Address to British Association, Section A.

after a finality of knowledge has been responsible for numerous fruitless speculations in the past, and it seems only too probable that the impatience of the mind with its own ignorance is the principal foundation of much of the theory of to-day. The satisfaction derived from the contemplation of simple and comprehensive laws may suffice perhaps to prove that the powers of the mind are limited, but hardly that the processes of nature are simple.

XLIV. *On the Specific Heat of Basalt.* *By* W. C. Roberts-Austen, *C.B., F.R.S., and* A. W. Rücker, *F.R.S.**

HAVING been asked by the Rev. O. Fisher to determine for him the latent heat of basalt, we made some experiments on a specimen which was furnished to us by Prof. Judd.

Fragments of the rock were melted in a platinum crucible, and the junction of a thermal couple consisting of platinum with platinum containing 10 per cent. of rhodium was immersed in the pasty mass, which was then allowed to cool. The scale of the galvanometer had previously been standardized by an observation on the solidifying-point of pure gold, and the pyrometer was standardized from time to time by the same means. When the index spot of light reached the desired point the wires were nipped off close to the basalt, and the crucible and its contents were plunged into 1000 grams of water contained in a silver calorimeter. The water was stirred by a screw or fan of silver which was rotated by an electric motor. The temperature was read by means of a mercurial thermometer which had been carefully corrected.

The two main sources of error in the experiments are probably an uncertainty as to the mean temperature of the basaltic mass owing to its being a bad conductor of heat, and the fact that in the processes of heating and cooling it undergoes more or less important changes of constitution.

The first error was reduced to small proportions by using small quantities of basalt, the mass employed rarely much exceeding 20 grams.

The second error is in part unavoidable. The rapidly cooled basalt was always glassy like olivine. We also found that frequent heatings and coolings, and the nature of the flame—whether oxidizing or reducing—employed to heat the mass appeared to affect the results very seriously.

In some experiments the crucible was heated in the flame

* Communicated by the Authors.

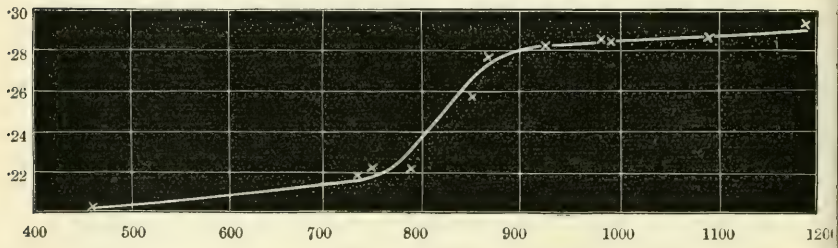
of a small gas-furnace, in others in a coke-furnace. All the former were consistent with each other, and those of the latter group in which fresh specimens of basalt were used were in agreement with them. The results obtained with specimens which had been heated two or more times in the coke-furnace were, however, very irregular, and have been discarded.

As we have not definitely proved what was the cause of these discrepancies, we publish our conclusions with a certain amount of reserve.

In the following table T is the temperature (Cent.) of the basalt at the moment of immersion, C is the mean specific heat between about 20° C and T.

T.	C.	T.	C.
467	0·199	860	0·277
747	·217	924	·282
759	·223	977	·284
792	·220	983	·283
846	·257	1090	·285
		1192	·290

These results are plotted in the figure.



If C_{12} be the mean specific heat between two temperatures t_1 and t_2 we have the relation

$$C_{13}(t_3-t_1)=C_{12}(t_2-t_1)+C_{23}(t_3-t_2).$$

If, then, we take the mean specific heat from 20° C.

to 470° to be ·199
to 750 „ ·216
to 880 „ ·278
and to 1190 „ ·290

we get the following results :—

The mean specific heat between

20 °	and	470°	is	0·199
470	and	750	is	·243
750	and	880	is	·626
880	and	1190	is	·323.

As Mr. Fisher was anxious to use our results in some calculations, we supplied him with approximate numbers before all our observations were completed. They do not, however, differ much from the above.

The general result seems to be that the specific heat of basalt follows the ordinary rule that the specific heat of a substance is greater in the liquid than in the solid state. There is a large absorption of heat in the neighbourhood of 800°, which raises the mean specific heat between 750° and 880° to the large value of 0·636.

XLV. *The New Theories of Solution.*

By James Walker, *D.Sc., Ph.D., F.R.S.E.**

SINCE the theories of osmotic pressure and of electrolytic dissociation were in 1887 made generally accessible by their publication in the *Zeitschrift für physikalische Chemie*, they have in Germany and elsewhere on the Continent enjoyed an ever-increasing favour and popularity. In this country they have mostly been met with a passive resistance; but in one or two cases where they conflict with rival theories they have encountered active opposition.

Mr. S. U. Pickering, in particular, has subjected them to unfavourable criticism, in the pages of this Magazine, at the Leeds meeting of the British Association, and elsewhere. His attack is twofold. In the case of osmotic pressure he compares the deductions from theory with the results of experiment, and endeavours to show discordance between them: against the dissociation hypothesis he seeks to raise "theoretical objections of a fundamental character."

First, with regard to osmotic pressure, Mr. Pickering singles out the freezing-point of solutions from the many phenomena which have received an explanation from this theory†, as the ground for his attack. The hypothesis of

* Communicated by the Author.

† Taking the osmotic-pressure theory in conjunction with his own, Arrhenius (Phil. Mag. xxviii. p. 36) enumerates seventeen heads under which these phenomena may be arranged—a number already too small to include the later researches of Nernst and others on solutions.

osmotic pressure claims to put us in a position to calculate the freezing-point of a dilute solution if we know its composition, the molecular weight of the substance in solution, and certain easily determined physical constants of the solvent—*provided that the solution is not an electrolyte*. If the solution conducts electricity, then, in order to find its freezing-point, we must in addition to the above data know its electrical conductivity; from which, by the help of the theory of electrolytic dissociation, we may calculate the correcting factor to be applied to the value deduced directly from osmotic pressure. A specimen showing how such a calculation is made will be given in the sequel. Mr. Pickering contends that the results of experiment are not in harmony with the values given by the theory; and this is perfectly true as regards the values calculated by Mr. Pickering. But then he has repeatedly confounded the laws deduced from van 't Hoff's theory with the empirical relations stated by Raoult; and, besides, has utterly ignored electrolytic dissociation in his calculations. He says (Chem. News, lxiii. p. 171):—"Professor Arrhenius accuses me of neglecting the effect of dissociation when discussing the freezing-points. In this he is quite right, for I do not believe in it." Of course, the assumption of such an attitude will undoubtedly enable Mr. Pickering to find disagreement on comparing experiment with calculation; but, if the comparison is to be of any value, it is surely evident that the theoretical numbers must be legitimate deductions from the theory as expounded by its originators, not as misconceived or distorted by its critics.

Before proceeding further, we shall do well to look for a moment at the conditions under which the law for the lowering of the freezing-point is obtained from the hypothesis of osmotic pressure. First of all, it must be understood that the solutions considered are dilute; secondly, that they do not conduct electricity; and, lastly, it is assumed that when a solution freezes, the pure solvent alone separates out in the solid form. If these conditions are fulfilled, it follows from the theory that the depression produced by one molecular weight of a substance (in grams) dissolved in 1000 grams of solvent, will be constant for any one solvent, and equal to $\frac{\cdot 002T^2}{W}$, where T is the freezing-point in the absolute scale, and W the heat of fusion of the solvent (van 't Hoff, Phil. Mag. xxvi. p. 95). Further, it follows that the depression of the freezing-point is proportional to the concentration of the solution (Blagden's Law). That this law is a well-justified generalization where dilute non-electrolytic solutions are concerned, is amply

proved by the agreement between experimental results and the values calculated directly or indirectly by its aid. Mr. Pickering, however, has made a number of accurate observations on the freezing-points of dilute solutions, and states that the numbers obtained by him are in discordance with those demanded by the law. The solvent he employed was water: the substances dissolved were sulphuric acid, calcium nitrate, calcium chloride, and alcohol. A table of the deviation of these solutions from regularity, *i. e.* from Blagden's Law, is given by Mr. Pickering in 'Nature,' vol. xlii. p. 629 (also in B. A. Reports, 1890, p. 316). It will be observed that only the solution of alcohol is a non-electrolyte, and therefore it only can be expected to give results in conformity with the law in question. Now in Mr. Pickering's table for dilute solutions the freezing-point of the aqueous alcohol shows a *maximum* deviation from regularity of 0°·0035, a result which might indeed seem to confirm the theory rather than contradict it. Mr. Pickering, however, estimates his mean error at 0°·0005, a seventh part of the above amount. This is somewhat strange; for on the same page where the claim to such accuracy is first made (Chem. Soc. Journ. lvii. p. 335) he compares two series of observations, made with different instruments, with the following result*:—

P. c. H_2SO_4.	Freezing-point.		Difference.
	Series I.	Series II.	
0·05	−0°·0260	−0°·0263	+·0003
0·10	·0515	·0492	−·0023
0·20	·0899	·0911	+·0012
0·50	·2135 (?)	·2054	+·0009
1·00	·4090	·4018	−·0072
1·50	·5896	·5846 (?)	−·0059

The values for the two series are deduced from the "smoothed" curves drawn to represent them, *i. e.* errors of individual experiments are already as far as possible eliminated. Yet if we add up the differences without regard to sign, and divide by their number, we find a mean difference of 0°·003. The result is quite the same if we compare the two series at closer intervals, twenty corresponding points on the two curves giving a mean difference of 0°·0033. Thus the only evidence that Mr. Pickering places before us from which we can form

* There are evidently some misprints in this table; I have taken the differences as being correct.

an independent judgment of his accuracy, shows his mean error in any one set of determinations to be many times greater than his own estimate of it. The maximum deviation exhibited by alcohol now falls within the magnitude of the experimental error; and thus Mr. Pickering's observations must be looked upon as furnishing one more confirmation of Blagden's Law and of van 't Hoff's theory.

With regard to the other three solutions, they cannot be expected to follow this simple law, if the theory of electrolytic dissociation is true. The theory, however, when applied in conjunction with van 't Hoff's expression for the molecular lowering, given above, enables us to calculate the freezing-point of dilute electrolytic solutions provided we know their conductivity. Now very accurate determinations of the conductivity of dilute solutions have been made by Kohlrausch, and from these Dr. Arrhenius has been at the pains to calculate the freezing-points of the solutions studied by Mr. Pickering, in order that a comparison might be instituted between the theoretical and the experimental numbers. A table embodying the results is given in the B. A. Report, 1890, p. 325 (Chem. News, lxiii. p. 148), and from it will be seen that the agreement in the case of weak solutions is as satisfactory as could be wished for. Arrhenius has there indicated the method of calculation, but it may be well that the matter should be looked into in somewhat greater detail, so that it may serve as an example of how such calculations are made, and show on what exceedingly simple principles they rest.

We find from van 't Hoff's formula that a normal aqueous solution of a non-electrolyte, *i. e.* a solution containing one molecular weight (in grams) per litre, freezes at $-1°{\cdot}90$. But sulphuric-acid solutions conduct electricity readily, which means, in the light of Arrhenius's theory, that the molecules are to a great extent dissociated into charged molecules $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{SO}_4}$. Each original molecule on dissociation gives three charged molecules ($\mathrm{H_2SO_4} = \overset{+}{\mathrm{H}} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{SO}_4}$), which act, as far as the freezing-point is concerned, exactly like any other molecules. If the whole of the sulphuric acid in a normal solution were thus dissociated, the freezing-point would be, not $-1°{\cdot}90$, but $-1°{\cdot}90 \times 3 = -5°{\cdot}70$. We know, however, that this is not the case, and that the dissociation varies with the dilution; so that it remains to determine the dissociated proportion of the sulphuric acid at the various concentrations. According to the theory this is given by the ratio of the molecular conductivity of the substance in a given solution

(μ_v) to its molecular conductivity in an infinitely dilute solution (μ_∞), *i. e.* in one where it is completely dissociated*. If the dissociated proportion is $\alpha\left(=\frac{\mu_v}{\mu_\infty}\right)$, then for every molecule which would be present if no dissociation took place, there are now actually $1+2\alpha$ molecules; for each original molecule on dissociation becomes three, *i. e.* contributes two additional molecules. We must, therefore, multiply the freezing-point as deduced from the theory of osmotic pressure by the factor $i=1+2\alpha$ determined for each concentration. Kohlrausch's results give us both μ_v and μ_∞. His estimate of μ_∞ for $\frac{1}{2}H_2SO_4$ as $370/10^7$ Siemens units is admittedly only a rough one, for the molecular conductivity for infinite dilution is difficult to determine in the case of many acids and bases. It is quite definite, however, with salts; and by applying the dissociation theory we can deduce μ_∞ for $\frac{1}{2}H_2SO_4$ with great accuracy from μ_∞ for $\frac{1}{2}K_2SO_4$, the difference between the values for potassium and hydrogen salts being constant according to the theory. The number thus obtained is $356/10^7$, and with it the accordance between experiment and theory is complete.

With respect to the deviations from constancy shown by stronger solutions, Mr. Pickering states that on the osmotic-pressure theory the depression of the freezing-point in their case should be abnormally small. This conclusion is reached from somewhat crude mechanical considerations regarding the balance of attraction between the solvent and the dissolved molecules (Journ. Chem. Soc. lvii. pp. 354, 355; Phil. Mag. xxix. p. 500). The matter is not nearly so simple as Mr. Pickering imagines. Even in the case of true gases (oxygen, nitrogen, &c.) there is a deviation from Boyle's Law, first in one direction and then in the other, as more and more gas is compressed into a given volume. In a solution the relations are much more complex, and it is impossible at present to predict what the behaviour of any particular substance in solution will be with regard to osmotic pressure (and the freezing-point) when the concentration passes beyond certain limits†. Mr. Pickering commits a strange mistake when he writes the following sentence (Chem. News, lxiii. p. 171):—"It is also remarkable that Professor Arrhenius should be so anxious to show that strong solutions have an abnormally high freezing-point, *since he starts by telling us that according to the*

* *Cf.* Ostwald, Outlines of General Chemistry, p. 285.

† Information on this point will be found in a paper by A. A. Noyes, *Zeitschr. physikal. Chem.* v. p. 53.

physical theory the reverse should be the case." Nowhere has Arrhenius made any such statement : the deviation may be in one direction or the other, depending on the nature of the dissolved body and of the solvent.

The objections urged by Mr. Pickering against the theory of osmotic pressure in the Philosophical Magazine, xxix. pp. 490–501, fall to the ground when we take into account his neglect of electrolytic dissociation, his (then) ignorance of the difference between Raoult's empirical value for the molecular depression and the value deduced from van 't Hoff's theory, and the odd selection of solvents to which Mr. Shaw drew attention at the B. A. meeting (Report, 1890, p. 336). We are given, for example, the molecular depression for water dissolved in H_2SO_4,H_2O. One is inclined to look upon the addition of water to this substance rather as the dilution of a strong sulphuric-acid solution than as the dissolution of water in a definite solvent. That such a hydrate as H_2SO_4,H_2O can be crystallized is no proof that it has previously existed as such in solution. All experiments, for instance, have gone to show that racemic acid and racemates do not exist in aqueous solution although they are always obtained on evaporation. Again, although ammonium chloride may be sublimed unchanged, yet it does not exist as such in the vaporous state. The fact, therefore, that certain hydrates can be obtained as crystalline solids in nowise proves their existence in solutions from which they separate ; so that Mr. Pickering's choice of them for solvents renders his experimental results in their application to the new theories worthless*.

Mr. Pickering takes exception to the theory of dissociation into ions on the ground that it "seems to be quite irreconcilable with our ideas of the relative stability of various bodies,

* In a footnote to the paper cited, p. 494, the following passage occurs :—"Van 't Hoff's statement as to Raoult's position respecting the high and low values of substances in water is certainly remarkable; he says (Phil. Mag. 1888, xxvi. p. 99), 'Raoult did not discover the existence of so-called normal [meaning small] molecular depression of freezing-point and lowering of vapour-pressure until he investigated organic compounds; their behaviour is almost without exception regular.' As a matter of fact, Raoult investigated organic substances *first* . . . . ." In this Mr. Pickering is perfectly accurate. The misunderstanding has arisen from a somewhat ambiguous German sentence of which the above is a translation: it runs—"so wurde auch die Existenz der sogenannten normalen molekularen Gefrierpunktserniedrigung und Dampfdruckverminderung erst aufgefunden, als Raoult sich den organischen Verbindungen zuwandte : da eben tritt das normale Verhalten fast ausnahmslos ein" (*Zeit. physikal. Chem.* i. p. 501). The meaning is of course—"the existence of so-called normal depression . . . . was not discovered until organic compounds were investigated" (by Raoult).

and with the principle of the conservation of energy." It is a curious fact, and one not without a certain significance, that it has been left to chemists to discover that the dissociation theory is at variance with the fundamental principles of energy, while physicists, on the other hand, have preferred to base their objections on more or less purely chemical grounds. Prof. Oliver Lodge, for example, refers to "that extreme state of dissociation which physically seems to be so satisfactory and chemically so abhorrent" (Brit. Assoc. Report, 1890, p. 331). Surely if the theory is such as to satisfy so eminent an authority as Prof. Lodge on the physical side, Mr. Pickering need not concern himself to show that it is in contradiction to the fundamental laws of energy. What it contradicts is Mr. Pickering's preconceived ideas of the nature of atoms and molecules and the energy associated with them*.

In his criticism in the July number of this Magazine (p. 21) Mr. Pickering lays great stress on the fact that the supporters of the dissociation theory sometimes speak of the heat of electrolytic dissociation as being positive, sometimes as being negative. Arrhenius, in his original paper (1884), stated that heat was absorbed on dissociation; whereas "they now hold, I believe, that the decomposition of molecules into ions *evolves* heat." "This change of front must rather be inferred directly from the writings of dissociationists than from any definite retraction which they have published; nor does it appear to have been followed by all the supporters of the theory. . . . . It may also be remarked that up to July 1889 Ostwald seems to have held both views, and to have adopted either just as the exigencies of the case suggested. . . . The first point, therefore, on which the dissociationists should give us definite information is whether dissociation of a molecule into its ions is supposed to evolve or to absorb heat." If Mr. Pickering had not been more zealous to criticise the dissociation theory than to properly comprehend it, he would scarcely have written these sentences. Two years ago, in the recognized organ of the "dissociationists" (*Zeitschr. physikal.*

* That Mr. Pickering is occasionally liable to mistake divergencies from his own opinions for contradictions to the "recognized principles of science" may also be seen in his paper "On Chemical Action" ('Nature,' xliii. p. 165), where he accuses thermochemists of implying that "physical changes are not subservient to the law of the conservation of energy." He assumes that all chemical reactions must be accompanied by evolution of heat, and explains the known exceptions to this arbitrary principle by introducing dissociation as an accessory process in endothermic reactions. This explanation, given by Berthelot (*Mécanique Chimique*, ii. p. 452), is rejected by Horstmann (*Physikalische Chemie*, vol. i. part 2 of Graham-Otto's *Lehrbuch*) and others as unnecessary.

Chem. iv. p. 96), Arrhenius published a paper on this very subject under the title "Ueber die Dissociationswärme und den Einfluss der Temperatur auf den Dissociationsgrad der Elektrolyte;" yet of the existence of this important memoir Mr. Pickering is completely ignorant, although an abstract of the results is contained in the Brit. Assoc. Report, 1890, pp. 220–223. In it the whole subject is discussed in great detail, numerical values being given for the heat of dissociation in nearly thirty instances. Some of them are positive, some negative, and mostly all are small. One of the most striking, if not one of the main, points in this paper is the prediction given by the dissociation theory of the existence of (hitherto unknown) electrolytic solutions with negative temperature-coefficients for the conductivity, and the perfect fulfilment of the prediction in the cases investigated (Brit. Assoc. Report, 1890, p. 223; Sack, Wied. *Ann.* xliii. p. 212).

A few paragraphs further on (p. 23) it is asked:—"How can it be maintained that the positive electrification of the hydrogen and the negative electrification of the chlorine would dissolve the union between them? . . . . . Further, if these so-called + and − charges repel each other, why are they attracted by the − and + charges respectively on electrodes during electrolysis? . . . . . On the new theory, the electric charges are the *cause* of decomposition." Here, again, there are put into the mouths of the dissociationists words which they never uttered. No one has stated that the electrical charges are the *cause* of dissociation, although they always accompany the phenomenon; nor has any one ventured to assert that the + and − charges repel each other,—in fact, the assumption that they attract each other as usual is the basis on which Nernst has built his elegant theory of the diffusion &c. of salt-solutions (*Zeitschr. physikal. Chem.* ii. p. 617). In a completely dissociated solution—one of hydrochloric acid let us assume—the positive and negative atoms are no longer paired off together, but there is rather supposed to exist a complete communism amongst the charged atoms. The positive ions ($\overset{+}{\mathrm{H}}$) still attract the negative ions ($\overset{-}{\mathrm{Cl}}$), but one hydrogen ion no longer exhausts all its attraction on one chlorine ion. There is rather, now, attraction between it and all the chlorine ions in its neighbourhood; and, similarly, any one chlorine ion is attracted in all possible directions by the hydrogen ions surrounding it. It is only when the positive ions are separated *en bloc* from the negative ions, that the electrostatic forces between the opposite kinds of electricity become evident.

After discussing the Clausius-Williamson hypothesis from

the *à priori* standpoint, Mr. Pickering goes on to say (*loc. cit.* p. 26) : "It does not seem necessary, however, to imagine the presence of free atoms to explain the phenomena of electrolysis (*cf.* Lodge, Brit. Assoc. Report, 1887, p. 338)." At the place cited, and more fully in his 'Modern Views of Electricity,' p. 80, Prof. Lodge gives as his opinion that "the addition of the idea of double-decomposition and interchange to the original hypothesis of Grotthus explains all that is required by the facts, viz. a virtual or potential dissociation, a momentary state of hovering and indecision, without the need for any continuous and actual dissociation."

It appears to me that such a potential dissociation is not quite sufficient to explain the known facts of the behaviour of electrolytic solutions. The state of hovering or indecision can only be brought about, according to the theory, by the approach of two molecules of the electrolyte to such a distance that they can interchange radicals. The number of molecules whose radicals are in this undecided state is therefore dependent on the number of molecular collisions per unit time, the word collision being used to express a conjunction of molecules close enough for atomic interchange to take place. On the other hand, the conductivity depends directly on the number of potential interchanges, and therefore on the number of collisions. Now in very dilute solutions the speed of the ions cannot be supposed to be altered by any increase in the dilution, and therefore the conductivity will be regulated by the number of collisions alone. In such salt-solutions as Kohlrausch investigated, where 1 gram-molecular-weight of salt was dissolved in as much as 100,000 litres of water (*i. e.* where there was only one molecule of salt to 5,500,000 molecules of water*), it was found that the conductivity is proportional to the concentration. But halving the concentration (*i. e.* the number of salt-molecules in a given volume) would diminish the number of collisions of the salt-molecules to a quarter of the former value. We should, therefore, expect on the potential-dissociation hypothesis that in dilute solutions the conductivity should be proportional, not to the concentration, but to the square of the concentration, which is not the case. On this ground, then, we must reject, I think, the idea of virtual dissociation brought about by atomic interchange. It might be contended that collisions of the salt-molecules with the water-molecules would be sufficient to cause the potential dissociation ; but if that were so, sodium hydrate and hydrochloric acid would always exist in a solution of common salt,

* It is here assumed that the molecule of liquid water is the same as that of water-vapour—probably it is twice as large.

and could be separated by diffusion or otherwise, which is contrary to all experience. The assumption of a merely potential dissociation thus fails to account for the known facts, whereas an actual dissociation at once affords the necessary explanation. Many interesting examples of the application of the dissociation theory to explain the electrical behaviour of salt-solutions are to be found in a paper by Ostwald, in the *Zeitschr. physikal. Chem.* ii. p. 270.

With reference to the existence of hydrates in solution, Mr. Pickering (Phil. Mag. xxxii. p. 91) brings against Mr. S. Lupton the charge of entirely ignoring the cumulative character of the evidence brought forward in favour of the hydrate hypothesis. Now this cumulative character of the evidence is precisely on what the theories of osmotic pressure and of electrolytic dissociation chiefly rely, and what Mr. Pickering altogether neglects. In the short paper by Arrhenius already referred to (Phil. Mag. xxviii. p. 36) attention is drawn to the great number of subjects dealt with by these theories jointly: in almost all cases a quantitative comparison of the results of experiment with deductions from the theory has been possible, with the most satisfactory results.

The only rival hypothesis which has been actively pursued is the hydrate theory, according to which the dissolved substance in an aqueous solution is combined with all the water (except in very dilute solutions) to form one or more hydrates. This is of course a perfectly legitimate hypothesis so far as it goes; but besides suffering at present from a slight arbitrariness in its employment where the interpretation of experimental data is in question, it also labours under the disadvantage of being unable to afford any secure basis for calculation. Mr. Pickering, it is true, has calculated the freezing-points of sulphuric-acid solutions by its aid, and on account of the apparent great elasticity of his method has obtained results in perfect accord with his experiments (Brit. Assoc. Report, 1890, p. 321; 'Nature,' xlii. p. 631). When one looks, however, a little closely into the details of the calculation, the concordance appears of questionable value. He attributes the lowering produced by the dissolved substance to three distinct causes, which he classifies as (1) mechanical, (2) physical, and (3) chemical. The actual depression is made equal to the sum of three components depending on the above causes. First of all, we have the mechanical lowering based on Person's so-called absolute zero for liquids, *i. e.* the temperature below which a liquid will not solidify (Proc. Chem. Soc. 1889–90, p. 150). Mr. Pickering himself has subsequently proved Person's views to be utterly untenable

(Proc. Roy. Soc. xlix. p. 11), so the mechanical depression is robbed of its basis. The physical and chemical lowerings are arrived at from a thorough confusion of heat with temperature. "A definite hydrate, such as H_2SO_4, $13H_2O$, can only give up its water by decomposing into the next lower hydrate, H_2SO_4, $9H_2O$ in the instance taken: the heat absorbed in this change is given by the heat of dissolution curve (863 cal.), and will lower the temperature of a mixture with a heat-capacity of 223·5 cal. by 3°·5" (Proc. Chem. Soc. 1889, p. 151). This 3°·5 is the "chemical lowering." Now while it may be true that the absorption of 863 cal. "will lower the temperature of a mixture with a heat-capacity of 223·5 cal. by 3°·5," it is difficult to see what this has to do with the freezing-point of sulphuric-acid solutions. The freezing-point of an aqueous solution is the temperature at which it is in equilibrium with ice; and no matter what amount of heat may be developed on the congelation, this temperature will remain unaffected. Heat, whether from an external or an internal source, cannot affect the temperature of equilibrium between the solid and the liquid: it can only change in the one case the relative proportions of the substances, and in the other the latent heat of fusion. Calculations on such a theoretical foundation need scarcely be further considered.

Whatever of future development may await the hydrate theory, it cannot to-day be looked upon as a serious rival to the hypotheses of osmotic pressure and electrolytic dissociation, the list of whose achievements is constantly increasing.

University of Edinburgh,
August 1891.

XLVI. *On a New Modification of Phosphorus.*

By H. M. Vernon, *Scholar of Merton College, Oxford**.

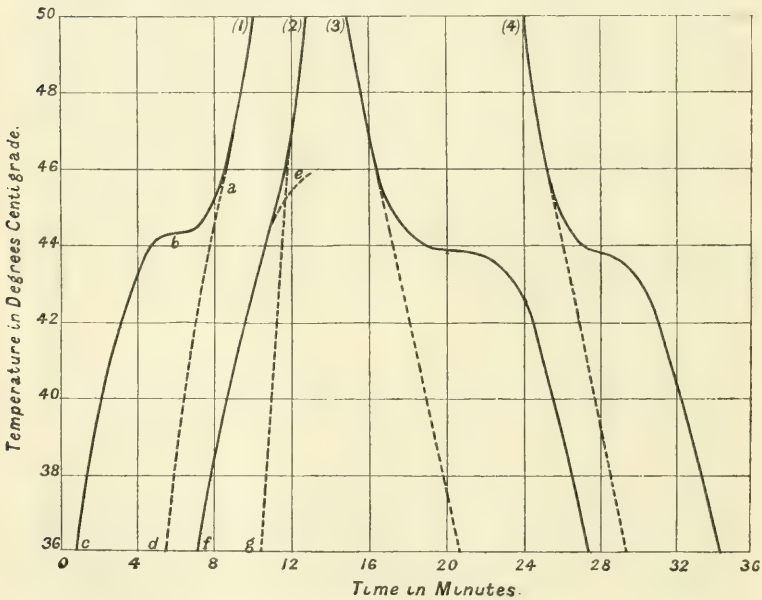
HAVING occasion to melt some ordinary yellow phosphorus, it was noticed that in some cases the phosphorus melted suddenly, and had no definitely marked melting-point, while in other cases it exhibited a definite melting-point, as most other bodies do when passing from the solid to the liquid state. Further examination confirmed this, and showed that these were two different crystalline varieties of phosphorus, which differed in other properties as well.

In order to examine the manner in which the phosphorus passed from the solid to the liquid state, quantities of about twenty-five grams were placed in a bulb-tube or broad test-

* Communicated by the Author.

tube and a thermometer placed in it. In all experiments on the rate of rise of temperature of the phosphorus, the tube was placed in an air-bath kept at 100° by being surrounded with boiling water. The tube of phosphorus was closed and the thermometer kept in position by means of a cork at the mouth; but no especial precaution was taken to make this tight to prevent air getting to the phosphorus, as a few drops of water forming a layer about 1 millim. thick were always introduced into the tube, and this effectually stopped any oxidation or combustion of the phosphorus, even when it was heated to 100°. In a few cases a thin layer of oil was substituted for the water. The thermometer was graduated in tenths of a degree, and as all readings were taken with a cathetometer, it was read to a hundredth of a degree. The temperature was read at intervals of a quarter or half a minute.

The first curve in the figure shows the rate of rise of tem-



perature of phosphorus with a well-defined melting-point. The melting-point of this variety was found to be 44°·3, a value found also by v. Schrötter and other observers for octahedral phosphorus. The second curve shows the rate of rise of temperature of the other variety of phosphorus. It will be seen that there is no sudden change in the form of the curve at any point, and so it might be thought to be impossible to

determine the melting-point. The direction of the lower part of the curve is, however, different from that of the curve from about 46° upwards; and if these two parts of the curve be produced in their same directions, the point where they meet will approximately indicate what may be taken as the melting-point of the phosphorus. The melting-point thus found is 45°·3, or a degree above that of the other variety. It may be wondered where all the latent heat of fusion of this phosphorus has disappeared to. On producing the upper parts of the curves of both varieties of phosphorus, it will be seen that the amount of heat required to melt them, which is represented by the area of the figures *a b c d*, *e f g*, is considerable in each case, though it is greatest for the variety with the definite melting-point. With the variety with the undefined melting-point, however, the latent heat of fusion begins to be absorbed at about 38° or lower, and being spread over such a large temperature-interval its effect is at first sight masked.

As these two different varieties of phosphorus were both obtained from the same specimen, supposed to contain phosphorus all in the same state, it is evident that it must be possible to easily convert one variety into the other. After a great many attempts had been made at converting them into one another by heating them to different temperatures, it was at length found that the modification into which the phosphorus solidified depended only on the manner of its solidification. If it cooled to below its solidification-point and then solidified, the temperature being thereby raised considerably, the variety with the undefined melting-point was formed; while if it began to solidify the moment it reached its solidification-point without cooling below it, the variety with the definite melting-point was formed. In order to cool it below 43°·8, the temperature of solidification, without solidification taking place, the tube containing the liquid phosphorus covered over with a layer of water or oil is placed in hot water, and the whole left to cool. The phosphorus generally cools to about 30° before solidification, and then the temperature rushes up to about 43°, or higher if the mass of phosphorus be large enough. To produce the other variety, the tube of melted phosphorus is plunged into cold water. The sides of the tube thus become cold enough to solidify some of the phosphorus, which causes the whole mass to solidify when it cools to 43°·8. The same effect may be produced by introducing some solid phosphorus into the liquid at about 44°, or by scraping a glass rod against some fragments of glass previously added to the melted phosphorus.

A single rapid or slow cooling in this manner is not generally sufficient to wholly convert one variety of phosphorus

into the other, but it must be repeated another time in the slow cooling, and two or three times more in the rapid cooling. It is very easy to obtain an idea as to the proportions of each variety present in any specimen by taking its rate of rise of temperature, the form of the curve obtained being between those of the two given, and the melting-point also varying between the extremes 44°·3 and 45°·3. It is therefore possible by alternate rapid and slow cooling to convert phosphorus backwards and forwards from one variety to the other as often as is desired.

As a single rapid or slow cooling is not sufficient to wholly convert one variety into the other, it follows that the phosphorus, when melted, must also be in a different state in the two cases, thus differing from sulphur, with which, though there are several different crystalline states, there is only one liquid state.

Up to the present phosphorus has always been stated to crystallize in octahedral or rhombic dodecahedral crystals. It is necessary therefore to ascertain which of the above varieties crystallizes in this form, and in what form the other variety crystallizes. It was at first endeavoured to crystallize out the phosphorus from its solution in carbon disulphide. About equal volumes of carbon disulphide and phosphorus were mixed and the excess of carbon disulphide distilled off; but the solution, though left for some time, did not crystallize. It would probably be only possible to obtain good crystals by operating on very large quantities of material, as carbon disulphide dissolves about eighteen times its weight of phosphorus, and so the whole of the phosphorus would crystallize out by the evaporation of this very small quantity of carbon disulphide. Benzene only dissolves phosphorus to a slight extent, but it was found possible to obtain small crystals by first warming the benzene with the phosphorus to 40° and then allowing the solution to slowly cool down. All the operations were performed in sealed glass tubes with a bend in the middle, and after the crystals had been deposited in one limb the benzene was poured off into the other, the crystals being thus left free for examination. The tubes containing the crystals were then examined under a microscope with a power of ten diameters. The crystals from the modification with the undefined melting-point were observed distinctly to crystallize in rhombic prisms; but as, from their inflammable nature, it was not possible to examine them except in the glass tube, no measurements could be taken. Some of the crystals were in masses, with smaller crystals shooting out in different directions at right angles from the larger ones: none of the crystals were, however, more than about 5 millim. in

length. Some of them could be seen on end, and the lengths of these axes appeared to be in about the ratio 1 : 2. The crystals from the modification of phosphorus with the definite melting-point, on examination in the same way, were observed to consist of masses of octahedral crystals. In size they were scarcely as large as those of the preceding modification, but there was no difficulty in identifying them. It is thus concluded that it is the variety of phosphorus with the definite melting-point and crystallizing in octahedra which has previously been examined and described; while the variety with the undefined melting-point, crystallizing in rhombic prisms, is the modification not previously described.

As the different crystalline modifications of sulphur exhibit a marked difference in their specific gravities, that of octahedral sulphur being 2·02, and that of prismatic sulphur 1·97, a similar difference might be expected to obtain for phosphorus. The specific gravity was determined by first weighing about 20 grams of the phosphorus, cut in oblong lumps and well dried, in a small stoppered weighing-bottle, then filling up the bottle with distilled water and weighing again, and lastly weighing the bottle full of water only. All determinations were made at 13° C., and were compared with water at the same temperature. Two different specimens of the octahedral modification were found to have the specific gravities 1·8177 and 1·8184; while for two different specimens of the prismatic modification the values 1·8272 and 1·8254 were obtained. The discrepancy between these two last values is probably due to the fact of one specimen containing some of the other variety of phosphorus in it, so the extreme value, 1·8272, is probably the more correct. A sample of phosphorus known to contain both varieties had a specific gravity 1·8237. The difference between the specific gravities of the two modifications is about half a per cent. This is not nearly so great as that of the two varieties of sulphur, which is about two and a half per cent., but it is large enough to be easily appreciable. The phosphorus used in these determinations was generally only purified by shaking it with a hot solution of sulphuric acid and potassium bichromate. Some of it was also distilled, but no difference in specific gravity or other properties was observable, so the oxidizing agent alone is probably enough to remove any impurities existing in it.

As the curves for the rate of rise of temperature show a considerable difference in the latent heat of fusion of the two varieties of phosphorus, a corresponding difference ought to be exhibited in the amounts of heat given out on solidification. Curve (3) shows the rate of cooling of octahedral or definite-

melting-point phosphorus, while curve (4) shows the rate of cooling of the other variety: both these curves are for the cooling of equal quantities of phosphorus. It will be seen that there is an appreciable difference in the heat given out; and this too is to a great extent masked, as the rhombic modification, on solidifying without cooling previously to below its solidification-point, is converted to a great extent into the octahedral modification. This is also the reason why both modifications solidify at the same temperature, viz. 43°·8. This temperature may therefore be taken as the solidifying-point of the octahedral modification, while that of the other variety is not known. It must, however, be a temperature below and not above this point. In order to determine it accurately, it would be necessary to cool a very large quantity of liquid phosphorus to below this temperature and then cause it to solidify, and notice the temperature to which the thermometer rushed up. If only a moderate quantity of phosphorus, as fifty grams, were thus treated, the heat of solidification would not be sufficient to raise the temperature of the mass up to the true temperature of solidification.

The different properties of the two modifications of phosphorus may be summed up as follows:—

Octahedral modification.	*Rhombic modification.*
Has definite melting-point at 44°·3.	Has no well-defined melting-point: melts at about 45°·3.
Specific gravity at 13°, 1·8177.	Specific gravity at 13°, 1·8272.
Has considerably greater latent heat of fusion than rhombic variety.	Has less latent heat of fusion than octahedral variety, and it begins to absorb this at about 38°.
Formed from the rhombic variety by cooling rapidly.	Formed from the octahedral variety by cooling slowly, so that it cools below the solidification-point before solidification sets in.
Solidifies at 43°·8.	

The University Laboratory,
Oxford.

XLVII. *Experimental Determination of the Beats in the Vibrations of a Revolving Bell.* *By* James Walker, *M.A.*, *and* J. L. S. Hatton, *B.A.*, *Demonstrators at the Clarendon Laboratory, Oxford* *.

In a communication read before the British Association at Leeds, and in a paper published in the Proceedings of the Cambridge Philosophical Society (vol. vii. p. 101)

* Communicated by the Authors.

Mr. G. H. Bryan has given the mathematical theory of the rotation of the nodal meridians in a revolving cylinder or bell. According to his analysis, the number of beats per revolution due to this rotation of the nodal meridians is independent of the velocity of revolution, and is given in the case of two-dimensional oscillations by $2s(s^2-1)/(s^2+1)$, $2s$ being the number of nodal meridians, and in the general case by $2s(s^2+\lambda_s-1)/(s^2+\lambda_s+1)$, λ_s being a quantity which can never be negative.

Mr. Bryan's own experiments with two different champagne-glasses gave "about 2·6 and 2·2 beats per revolution respectively for the gravest tone," of which "the latter is too small to be compatible with" the theory, and it was at his suggestion that we have undertaken some experiments at the Clarendon Laboratory in order to test the same. The results already obtained appear of sufficient interest to warrant this preliminary note on the subject, pending a fuller investigation with more accurate apparatus.

The glass to be experimented upon was rigidly attached to the disk of a whirling-table carrying a graduated scale; and an index, which could be held in a fixed position in space, was carried round with the disk when released by the observer. The glass was caused to vibrate by means of a bow: when the note obtained was free from beats and of the required pitch the disk was rotated. In order to prevent complicating the experiment by the acceleration of the disk several beats were first observed, and when the intervals at which they occurred appeared to be uniform the index was released on hearing a beat, and after the observation of a certain number the disk was stopped. The whole number of turns were counted, and the position of the index when the disk was stopped gave the fraction of a turn.

In order to concentrate the sound and to prevent any motion of the ear during the observations, the beats were observed through a tube fixed with one extremity close to the revolving glass. A difficulty arose in obtaining glasses which gave a pure tone, and it was found that, even after careful selection of the glass, accuracy was only to be arrived at when the vibrations were excited with great care by means of a violin-bow. The glasses selected were bell-shaped.

The following were the results obtained, and it will be observed that in each case the mean is slightly above the value calculated from the two-dimensional theory.

Glass No. 1. Gravest tone c'''.

	Beats.	Revolutions.	Beats per Revolution.
Four nodes.			
	14	5·65	2·48
	14	5·7	2·46
	16	6·5	2·46
	10	4·0	2·5
	8	3·225	2·48
	10	4·0	2·5
	10	4·1	2·44
	12	4·77	2·52
	11	4·38	2·51
	17	7·0	2·43
			Mean... 2·48
Six nodes.			
	8	1·65	4·85
	8	1·64	4·88
	8	1·6	5·0
	9	1·87	4·81
	8	1·65	4·85
	8	1·65	4·85
	10	2·08	4·81
	10	2·12	4·72
	10	2·1	4·76
	8	1·65	4·85
			Mean... 4·84
Eight nodes.			
	8	1·08	7·41
	8	1·14	7·01
	8	1·1	7·27
	8	1·13	7·08
	8	1·1	7·27
	8	1·12	7·14
	8	1·12	7·14
	8	1·05	7·62
	8	1·08	7·41
	8	1·08	7·41
			Mean... 7·28

Number of Nodes.	Beats per Revolution.		Difference.
	Theory.	Experiment.	
4	2·4	2·48	·08
6	4·8	4·84	·04
8	7·005	7·28	·275

Glass No. 2. Gravest Tone g''.

	Beats.	Revolutions.	Beats per Revolution.
Four nodes.			
	9	3·75	2·4
	11	4·49	2·45
	12	4·92	2·44
	9	3·73	2·41
	12	4·87	2·46
	17	6·97	2·44
	14	5·59	2·5
	15	6·27	2·39
	11	4·47	2·46
	12	5·03	2·38
			Mean... 2·43
Six nodes.			
	11	2·29	4·8
	12	2·38	5·04
	10	2·12	4·71
	10	2·1	4·76
	9	1·87	4·81
	7	1·45	4·83
	8	1·66	4·82
	11	2·26	4·87
	9	1·84	4·89
	9	1·88	4·79
			Mean... 4·83
Eight nodes.			
	12	1·64	7·32
	15	2·11	7·11
	14	1·99	7·03
	13	1·88	6·91
	15	2·08	7·21
	14	1·94	7·22
	15	2·05	7·32
	12	1·67	7·18
	13	1·86	6·99
	19	2·69	7·06
			Mean... 7·15

Number of Nodes.	Beats per Revolution.		Difference.
	Theory.	Experiment.	
4	2·4	2·43	·03
6	4·8	4·83	·03
8	7·005	7·13	·125

These results afford, moreover, the means of determining in the case of a non-revolving bell the proportion of the whole kinetic energy which is due to the longitudinal components of the displacement, and thus give an indication of the extent to which the vibrations differ from two-dimensional vibrations on the one hand (in which the proportion is zero), and from the vibrations of a circular plate on the other hand (in which the proportion is unity).

For, according to Mr. Bryan's results, the kinetic energy in the case of a non-revolving bell is proportional to $(\lambda_s+1+s^2)p^2$, in which expression the term $\lambda_s p^2$ arises from the longitudinal motion, and hence the proportion in question is

$$\frac{\lambda_s}{\lambda_s+1+s^2}.$$

On the other hand, when the bell is rotated the number of beats per revolution is

$$2s\frac{\lambda_s+s^2-1}{\lambda_s+s^2+1}=n \text{ say},$$

whence we easily obtain

$$\frac{\lambda_s}{\lambda_s+1+s^2}=\frac{n(s^2+1)-2s(s^2-1)}{4s}.$$

Using the values given above for the number of beats per revolution in the case of the different modes of vibration of the two glasses, we obtain from the above formula the following results :—

Number of Nodes, $2s$.	Proportion of the whole kinetic energy which is due to longitudinal motion.	
	Glass No. 1.	Glass No. 2.
4	·05	·019
6	·033	·025
8	·232	·076

XLVIII. *On Periodic Motion of a Finite Conservative System.* *By* Sir William Thomson*.

1. In a recent communication to the Royal Society† I suggested an extension to stable systems in general of the well-known theory of "fundamental modes" for systems in which the potential energy is a quadratic function of coordinates and the kinetic energy a quadratic function of velocities, each with constant coefficients. This extension is the subject of the present communication to the British Association.

2. In its title, "finite" means that the number of freedoms is finite and that the distance between no two points of the system can increase without limit. "Conservative" means that the kinetic energy is always altered by the same difference when the system passes from either to the other of any two configurations, whatever be the amount given to it when the system is projected from any configuration and left to move off undisturbed. By "path of a system" we shall understand, in generalized dynamics, the succession of configurations through which the system passes in any actual motion: or the group of single lines constituting the paths traversed by all points of the system. By an "orbit" we shall understand a circuital path; or a "path" of which every constituent line is a complete circuit, and all moving points are always at corresponding points of their circuits at the same time.

3. It will be convenient, though not necessary, to occasionally use the expression, "potential energy of the system in any configuration." When used at all it shall mean the difference by which the kinetic energy is diminished when the system passes to the configuration considered, from *a* configuration or *the* configuration such that passage to any other permitted configuration involves diminution of the kinetic energy. By "total energy" of the system in any condition will be meant the sum of its kinetic and potential energies.

4. *Theorem of periodic motion.* For every given value, E, of the total energy, there is a fully determinate orbit such that if the system be set in motion along it, at any configuration of it, with the given total energy, E, it will circulate periodically in it.

* Communicated by the Author; §§ 1 ... 10, and §§ 17 ... 22 having been read before Section A of the British Association at its recent meeting in Cardiff.

† Proceedings, June 1891, "On some Test Cases for the Maxwell-Boltzmann Doctrine regarding Distribution of Energy."

5. To prove this theorem, suppose the number of freedoms to be i. Any configuration, Q, is fully specified by i given values for the i coordinates respectively. Suppose now the system to pass through some configuration, Q, at two times separated by an interval T, and to have the same velocities and directions of motion at those times. The path thus travelled in this interval is an orbit, and it is periodically travelled over in successive intervals each equal to T. To find how to procure fulfilment of our supposition, let the system be started from any configuration, Q, with any i values for the i velocity-components (or rates of variation per unit-time, of the i coordinates). To cause it to return to Q after some unknown time T, we have $i-1$ equations to be satisfied : and to cause $i-1$ of its velocity-components to have the same values at the second as at the first passage through Q we have $i-1$ equations to satisfy ; and, in virtue of the equation of energy, the remaining velocity-component also must have the same value at the two times. That the total energy may have the prescribed value, E, we have another equation. Thus we have in all $2i-1$ equations, among coordinates and velocity-components. Eliminate among these the i velocity-components, and there remain $i-1$ equations among the i coordinates which are the conditions necessary and sufficient to secure that Q is a configuration of an orbit of total energy E. Being $i-1$ equations among i coordinates, they leave only one freedom, that is to say they fully determine one path; of which, in the language of generalized analytical geometry, they are the equations. The or any path so determined is *an* orbit of total energy, E. Thus is proved the Theorem of § 4.

6. The solution of the determinate problem of finding an orbit whose total energy has the prescribed value, E, is, in general, infinitely multiple, with different periods for the infinite number of different orbits determined by it.

7. A simple illustration with only two freedoms, will help to the full understanding of § 6 for every case, of any number of variables. Consider a jointed double pendulum consisting of two rigid bodies, A and B : one (A) supported on a fixed horizontal axis, I ; the other (B) supported on a parallel axis, J, fixed relatively to A : and for simplicity let G, the centre of gravity of A, be in the plane of the two axes. Call H the centre of gravity of B. Let ϕ be the angle between the plane I J and the vertical plane through I, which we shall call I V ; and let ψ be the angle between the plane J H and the vertical. The coordinates and velocities of the system in any condition of motion are ϕ, ψ, $\dot{\phi}$, $\dot{\psi}$. The potential energy of the system, in kinetic units, will be $g\mathrm{W}z$, where W denotes the sum

of the masses, and z the height of their centre of gravity in any configuration of the system, above its lowest. Suppose now A to be placed in any particular position ϕ_0; and let it be required to find what must be the position, ψ_0, of B, and with what velocities, $\dot{\phi}_0, \dot{\psi}_0$ we must start A and B in motion, so that *the first time* ϕ has again the same value, ϕ_0, that is to say when A has made one complete turn in either direction, the system shall be wholly in the same position (ϕ_0, ψ_0) and moving with the same velocity $(\dot{\phi}_0, \dot{\psi}_0)$ (in the same direction understood) as at the beginning. This implies only two equations, $\psi = \psi_0$; and either $\dot{\psi} = \dot{\psi}_0$, or $\dot{\phi} = \dot{\phi}_0$ (because either of these implies the other in virtue of the equation of energy). And we have just two disposables, ψ_0, and either $\dot{\psi}_0$ or $\dot{\phi}_0$ (the given total energy E determining either $\dot{\phi}_0$ or $\dot{\psi}_0$ when the other is known). The solution of this determinate problem is clearly possible, *unless* E *is too small* : but it is not generally unique. We may have solutions with the velocities of A and B started each in the positive direction, or each negative, or one negative and the other positive. If A is a flywheel of very great moment of inertia, and B a comparatively small pendulum hung on a crank-pin attached to it, and if for simplicity we suppose the crank to be counterpoised, so that the centre of gravity of A is in its axis, it is clear that, according to the greater or less value given for E, B may turn round and round many times before A comes again to its primitive position ϕ_0. But it is clear that, though not generally unique, our problem of finding periodic motion with just one complete turn of A in its period has no real solution unless E is large enough ; has many solutions for large enough values of E; but has not an infinite number of solutions for any finite value of E.

8. Again, let the condition be that, not the first time, but the *second* time A passes through its initial position, both coordinates and both velocities have their primitive values. When the given value of the total energy is not too great, the periodic motion which we now have will be purely vibratory ; and the solution clearly duplex. But if E be great enough, A may still merely vibrate, while B may go round and round, first in one direction and then in the other, within the period of A's vibration. If the condition be that not at the first and not at the second, but at the third transit of A across its initial position, both coordinates and both velocities have their primitive values, we may, with sufficiently great total energy, have still wilder acrobatic performances, both bodies going round and round sometimes in one direction and sometimes

in the other. Still with any finite value for E there is only a finite number of modes for the motion subject to the condition that the third transit of A through its initial position completes the first period. Wilder and wilder vagaries we have to think of if the first period is completed at the fourth transit of A ; and so on.

9. This terrible Frankenstein of a problem is all involved in a very simple mathematical statement *not* including any declaration that it is the first, or the second, or the third, or other specified, transit of A that completes the first period. It will probably be convenient to arrange so as to find a transcendental equation which will have an infinite number of finite groups of roots equal to the periods of the modes of the periodic motions.

10. The case of no gravity presents a vastly simpler problem, of which the main solution has no doubt been many times found in terms of elliptic functions in the Cambridge Senate-house and Smith's Prize examinations. The character of the solution of this, as of all "adynamic" problems, is independent of the absolute value of the given energy, and of ϕ_0. It depends only on the value of the ratio $\dot{\psi}_0/\dot{\phi}_0$, which of course may be either positive or negative. In the general solution $\psi-\phi$ is clearly a periodic function of the time ; and our question of periodicity relatively to a *fixed* plane through I resolves itself into this :—During the period of the variation of $\psi-\phi$, is the change of ϕ either zero or a numeric commensurable with 2π? A corresponding question occurs for every case in which our "system" is free in space, without any fixed guides, and with no disturbing force from other bodies ; as, for example, in the question of rigorous periodicity of the motion of three bodies such as the earth, moon, and sun, or of any finite number of mutually attracting bodies, such as the solar system, to be considered presently.

11. An (idealized) ordinary clock with weight, and pendulum, and dead-beat escapement, affords an interesting illustration. For simplicity let the cord be perfectly flexible and inextensible ; let the cord-drum be rigidly fixed on the shaft of the escapement-wheel ; let the escapement be rigidly fixed to the pendulum ; and let the pendulum be a rigid body on perfect knife-edge bearings. Thus we have virtually two bodies, each with one freedom : A the escapement-wheel, cord, and weight ; B the escapement and pendulum. Each impact of tooth on escapement is, in every clock and watch, followed by a mutual recoil. This recoil probably in almost all practical cases goes so far as to produce complete separation, followed by several more impacts and recoils before the tooth escapes,

and the corresponding next tooth falls on the other side of the escapement. But there is a loss of energy by impacts and slipping, both on the non-working and on the working faces of the escapement. The loss on the working faces could be dispensed with: but the loss on the non-working faces is essential to the going of the clock. In our idealized clock we suppose each recoil to exactly reverse the relative motion of tooth and escapement in the direction perpendicular to the common tangent plane of the two surfaces at their point of impact; and we suppose the surfaces to be perfectly frictionless, so that the infinitely great mutual force at the instant of each impact is exactly in that direction. The jumping action thus produced would keep stopping the clock and letting it go on again: and would utterly prevent any regularity of going. Therefore I add the following arrangement of energy-receivers to annul the shocks on the non-working faces of the escapement:—Prolong the shaft of the escapement-wheel, and fix on it, in helical order, sixty little arms each carrying at its end a disk, with its front face in a plane through the axis. Adjust the escapement-wheel on its shaft, so that when each of its thirty teeth strikes one or other of the two branches of the escapement, the lowest one of those sixty disks has its front face vertical. On a horizontal plane below the prolongation of the shaft place sixty little balls (energy-receivers) in such positions that each shall be struck by a disk *just* before the corresponding tooth touches the corresponding branch of the escapement. Let the mass of each ball be equal to the proper inertia-equivalent* of A, (the escapement-wheel, &c., and driving-weight). Each ball struck by it, receives the whole kinetic energy which A had before the impact; and leaves A at rest, with a tooth of the escapement-wheel pressing on a non-working face of the escapement. Fix sixty rigid stops to prevent the balls from, in any circumstances, (§§ 13 ... 16), going too far behind the positions in which they are initially placed. Each of these stops must be slotted, to allow the proper disk of the escapement-shaft to strike the ball and afterwards pass clear through with its carrying arm. For brevity these forked stops will be called the home-stops. Fix also sixty other stops, (field-stops we shall call them) in such positions that the balls shall strike them all simultaneously and at exactly the instant (§ 12) when the weight strikes the bottom of the clock-case.

* Let r be the radius of the cord-drum: W the driving-weight: k the radius of gyration, and w the weight of the whole rotating body consisting of cord-drum, escapement-wheel, shaft, and 60 arms and disks: a the length of each arm reckoned from the axis to the point of its disk which strikes the ball. The "proper inertia-equivalent" is $(\mathrm{W}/r^2 + w/k^2)\, a^2$.

12. Suppose now the pendulum of our ideal clock, with its weight wound up very nearly to the top, to be started with sufficient range to let it keep going. For simplicity let this range be small enough to secure that when the weight is run down, the augmented range of vibration will still be within the limits allowed for proper action of the escapement mechanism. Let the bottom of the clock-case be a rigid horizontal plane fixed relatively to the framework bearing the wheel and pendulum in exactly such a position that when the weight, in running down, strikes it, the pendulum is at either end of its range. The weight jumps up after the impact, and the clock goes backwards, the energy-receivers return home from their field stops at exactly the right times, retracing exactly every step till the weight (wound up by the energy of the pendulum and of the returning energy-receivers) passes through its initial position. If it is allowed to go higher till it strikes against an unadjusted stop, the clock may be stopped for a time, with the pendulum vibrating through a moderately small range, and one tooth of the wheel chattering against one working facet of the escapement: but "sooner or later" (very soon) the tooth will escape; the clock will again go forward; the weight will run down, and again strike the bottom and jump from it, this time *not* when the pendulum is quite exactly at either end of its range.

13. Complicated but quite orderly action will follow; and "sooner or later" a tooth will be hooked up by the escapement and the clock will go backwards a beat or two; but after a very few beats, if more than one, it will go forward till the weight strikes the bottom again. "Sooner or later" the bottom will be struck at a time when the pendulum is *very nearly* at rest at either end of its range and when several energy-receivers are in such positions as to arrive home and strike disks at right times; and the clock will go backwards for a good many beats.

14. "Sooner or later," that is to say after some finite number of millions of millions of years, the weight will strike the bottom when the pendulum is *so very nearly* at rest at either end of its range and all the sixty balls so very nearly striking each its field-stop, that the clock will be driven back, winding up the weight till it again strikes the top stop, and immediately, or after a very few beats, begins again to go forward and let the weight run down. But our subject is not the fortuitous concourse of atoms. It is "periodic motion of a finite system."

15. Returning therefore to the end of § 12; let the top stop be so adjusted that it is struck by the weight at an instant

when the pendulum is at one end of its range. The clock instantly begins to go forward ; and goes on retracing every step, and repeating every one of the numerous impacts, of its first forward motion ; till the weight strikes the bottom exactly when each of the sixty balls is striking its field-stop, and when the pendulum is at one end of its range, the same end of its range as when the weight struck the bottom the first time. Thus a *perfectly* periodic motion goes on for ever.

16. During any of the half-periods in which the clock is going forward, and the weight running down, any moderate disturbance, such as a slight blow on the pendulum, or a holding of the escapement-wheel stopped for some time, large or small, will make no noticeable difference in the subsequent motion : till the weight reaches the bottom of its range, when we find that the periodicity is lost, and the state of things described in §§ 13, 14 supervenes. But any such disturbance during a half-period when the clock is going backwards causes the backward motion to cease and regular forward motion to follow, immediately, or after a few beats, a greater or less number according as the disturbance is exceedingly infinitesimal or but moderately small. This is a true dynamical illustration of the "dissipation of energy," and helps to show the vanity of attempts which have been made to found "Carnot's Principle," or "the Second Law of Thermodynamics," or theories of chemical action, on Lagrange's generalized equations of motion.

17. Consider the "problem of the three bodies," in two varieties ; first "the Lunar Theory," secondly "the Planetary Theory." One body (the Sun) is in each case vastly larger than either of the two others. In the first case the two others (the Earth and Moon) are so near one another in comparison with the Sun's distance from either that his force produces but a small disturbance of the relative motion of the Earth and Moon under their own mutual attraction. In the second case, two planets move each chiefly under the Sun's influence with comparatively small disturbance by their own mutual attraction. In each case we shall, for simplicity, neglect the motion of the Sun's centre of gravity, and consider him as an absolutely fixed "centre of force."

18. Taking first the lunar theory, suppose the centre of gravity, I, of Earth and Moon to move *very approximately* in a circle round the Sun. Now (without necessarily considering that the Moon is much smaller than the Earth) at an instant when the line M I E passes through S give equal and opposite momentums to M and E in the line M E so as to annul their relative motion in this line if they had any, and to cause each

to move exactly perpendicularly to it. If the next time their line passes through S they are again moving perpendicularly to M E, their motion relatively to S I is rigorously periodic. This we see by considering that if both motions are reversed at any instant, M and E will exactly retrace their paths; and if such a reversal is made at an instant of perpendicularly crossing the line S T, the retraced paths are similar to the direct paths which are traced when there is no reversal.

19. Hence if the three bodies be given in line, S M E, we secure rigorous periodicity of their motion if we project them in contrary directions perpendicular to this line with exactly such velocities that the next time M E is again in line with S, now S E M, their directions of motion are again perpendicular to E M. The problem of doing this has three solutions; in one of which the velocities of projection are so great that M and E are carried far away from one another, in opposite directions round the Sun till they again come near one another and in line on the far side of the Sun. Excluding this case we have certainly only two solutions left. In these I describes exceedingly nearly a circle round the Sun; while M and E move relatively to the point I and the line I S, somewhat approximately in circles, but to a second approximation in the ellipses corresponding to the lunar perturbation called the *variation*, and quite rigorously in two constant similar closed curves each differing very little from the variational ellipse. The centre of the variational ellipse is at I: its major axis is perpendicular to S I and exceeds the minor axis by approximately 1/179·6, being the square of the ratio (1/13·4) of the angular velocity of S I to the angular velocity of M E, each relative to an absolutely fixed direction. There are two solutions of this kind, in one of which (as in the actual case of Earth and Moon) E M turns samewards as, in the other contrary-wards to, S E.

20. If M E were two or three times as great as it is when the three bodies are in line, S M E, and other dimensions the same, we should still have a solution for periodicity corresponding to that of § 19, but with the orbital curves of M and S round I differing very largely from circles and largely from ellipses. When M E exceeds a certain limit, this kind of solution becomes impossible. It would be not wholly uninteresting to follow the character of the orbital curves round I for increasing magnitudes of M E until they are lost. The solution referred to and rejected in § 19 is still available and becomes now more interesting, but not so interesting as the corresponding solution in which M and E, now two planets, are projected so as to revolve in the same directions round the Sun.

21. *Rigorously periodic motion of two planets.* Given S V E in line, the Sun and two planets at distances such as those of Venus and the Earth :—it is required to project them with such velocities that the subsequent motion is rigorously periodic. A first solution is obtained by projecting them perpendicularly to V E with such velocities that their periods of revolution round S are approximately equal ; and exactly such that at the next time when V E is again in line with S, the motions are rigorously perpendicular to this line. The velocities which must be given to fulfil this condition must be such that the major axes of the ellipses approximately described are approximately equal. This solution, however, belongs rather to the Cometary than to the Planetary Theory.

22. Project the planets perpendicularly to S V E with such velocities that after some given number of times of their being in line with the Sun, their motions are, for the first time again, perpendicular to S V E. The determinate velocities which fulfil this condition must I think be such that the orbits are approximately ellipses of eccentricities not differing much from those required to make the major axes such that the periods have the proper commensurability to render the line of the three bodies at the second perpendicular crossing approximately coincident with their line at the initial perpendicular crossing.

Madeira, Sept. 8, 1891.

[To be continued.]

XLIX. *On some of the Effects of Magnetism on Rods of Iron, Nickel, and other Metals which have received a permanent Torsional Set ; and a new form of Chronograph Stylus.* By Frederick J. Smith, *Millard Lecturer Mech. and Phys., Trinity College, Oxford**.

DURING the present year I have gone through rather a long series of experiments with a view to discover some form of chronograph stylus which would respond to rapid vibrations and make a clear record of its vibrations on the moving plate of a chronograph. I have succeeded in finding a combination which appears to give satisfactory results. During the research several facts of interest bearing on a certain branch of magnetic induction presented themselves. I beg respectfully to give a summary of some of them in the

* Communicated by the Author.

form of short notes. In the last two notes will be found a description of the application of one of the phenomena to the production of a chronograph stylus. I have added below, a list of some of the papers which treat of relationships which exist between stress and electromagnetic induction.

1. In 1841 Joule showed that if an iron bar was magnetized it was increased in length; he also found that if an iron bar was subjected to considerable tension and then magnetized it was shortened. Since Joule's discovery the action of the force of magnetization on iron subjected to stress has been investigated by Matteucci, *Compt. Rend.* t. xxiv. p. 301 (1847); Wertheim, ibid. xxxv. p. 702 (1852); also *Ann de Chem. et de Phys.* [3], t. l. p. 385 (1857); Villari, Pogg. *Ann.* (1868); Wiedemann, *Galvanismus*, p. 447; Sir W. Thomson, Phil. Trans. 1879, p. 55; Prof. Hughes, Proc. R. S. (1881), xxxi. p. 524; id. ibid. xxxiii. p. 25; Mr. S. Bidwell, Proc. R. S. xi. p. 257 (1886); ditto. xlvii. p. 496; Prof. Ewing, Proc. Roy. Soc. vol. xxxvi. p. 117; 'Nature,' vols. xlii., xliii.

2. Wiedemann, *Galvanismus*. p. 447, showed that under certain conditions twisted iron wires untwist on magnetization. His words are :—"Die gedrillten Eisendrähte detordiren sich also bei der Magnetisirung." He made his experiments on an iron wire suspended in a vertical position and weighted with a considerable mass, viz. 1103 grammes. By means of a disk attached to it, and a cord and weight, torsion was given to the iron wire. A coil of copper wire, in the axis of which was the iron wire, was used for magnetizing the latter; change of torsion was read by means of a mirror and scale seen in the field of a telescope. In his experiments torsional *set* was *not* produced, or if so in only a very small degree. In my own work rods of iron, steel, and nickel which were *not* weighted and had received *permanent torsional set* were experimented on. The magnetizing force H used by me was many times greater than that used by Wiedemann; as far as I can calculate probably in some cases thirty-five times as great. I arrived at this conclusion by assuming his coil to have had next to no resistance, also that the whole number of cells mentioned were used by him.

3. The first experiment was arranged to find out whether a magnetic field of force acting on an iron rod only subject to its own weight would set up a torsional stress in it. The following apparatus was used :—A magnetizing coil 50 centim. long, wound on a glass tube 0·825 centim. external diameter; the number of turns of silk-covered copper wire 0·6 millim. diameter was 3865; the coil was wound so as to have no component along its length, its magnetizing force for one

ampere was $H=\frac{4\pi\times 3865\times 1}{50\times 10}=97{\cdot}1$ C.G.S. units. The coil was fixed vertically on a strong board. Under its lower end, at a distance of 4 centim., a brass frame was fixed carrying a mirror on an axle, the axis of which coincided with that of the coil. The rods to be examined were the same length as the coil but elongated at each end with nonmagnetic wire; these were passed through the coil and attached at one end to the axle of the mirror, which was used in conjunction with a telescope and scale. Any minute torsion of the rod could be accurately measured. The scale was placed at a distance of 226 centim. from the axis of the mirror, the wire was passed through collars within the tube; these kept it in a central position and prevented any movement sideways. By means of a liquid resistance in the circuit the current was regulated, so that the value of H could be easily changed.

4. The first iron rod which was tested was 50 centim. long and 0·162 centim. in diameter, well annealed by being placed in a tube furnace and raised to a bright red heat and cooled slowly. (All the metals were supplied by Messrs. Johnson and Matthey, and may be considered as pure as can be procured.) The reading of the scale as seen in the telescope was brought to zero, and then the rod was magnetized with a magnetizing force H of 21·5 C.G.S. units. A rotation of 0·1 centim. was produced in a direction with clock-hands to a person looking from the fixed end down the rod; when the current was broken it returned instantly to its initial position. A very delicate thermometer was put from time to time in the usual position of a rod under examination and then the current was put on as for an experiment; no change of temperature could be detected, so that the effect produced was due to the magnetizing force alone.

5. The rod in (4) was replaced by one which had received a permanent torsional set of seven revolutions. To give this amount of torsion the rod was fixed at one end and then the other was rotated through over eight complete revolutions, it was finally left with a twist of seven revolutions. The twist was with clock-hands to a person looking down the rod from the fixed end as an axis of the couple; it was then subjected to a force H=21·5. This instantly produced a further torsion in the *same* direction as the initial torsion of 5 scale-divisions. The scale (divided into centim. and millim.) was in this and all the following experiments 180 centim. from the mirror. The effect was carefully examined by several observers and always reproduced when required. In subsequent experiments I found that when the rotation was large it could be readily made visible by the addition of a light pointer attached to the

end of the axle of the mirror. This led to the result described in (25).

6. On reversing the current the direction of torsion was *not* reversed. A similar rod, with the same amount of torsion in the opposite direction, was further twisted by the magnetic force in the direction of the initial torsion. When the current was off, the rod returned to its original position. Subsequent experiments showed that there was a limit to this torsion by magnetism.

7. The next experiment was arranged to find out any relationship which might exist between the magnetizing force and the amount of torsion.

An iron rod 0·16 centim. diameter and 50 centim. long, with torsion as before (5), was successively magnetized with an increasing force, shown in the column headed H, the corresponding deflexions are shown in the next column.

H.	Deflexions.	H.	Deflexion.
19·02	3·0	114·12	10·1
28·53	4·0	123·63	10·1
38·04	5·2	133·14	10·1
47·55	6·1	142·65	10·1
57·06	7·1	152·16	10·1
66·57	8·0	161·67	10·1
76·08	8·8	171·18	10·1
85·59	9·1	180·69	9·0
95·10	10·0	190·20	9·0
104·61	10·0		

The table indicates that for low values of H the deflexion is nearly proportional to the force H, and that after a certain value it becomes permanent and then begins to fall off, indicating an untwisting. I am now arranging a large battery of accumulators for the production of very much more intense magnetic fields, so that I may find out the rate at which the wire untwists after the maximum of deflexion is reached.

The last experiment was repeated with a similar iron rod, subjected to one complete twist in its length instead of seven, and the following results were obtained :—

H.	Deflexions.	H.	Deflexions.
28·53	1·0	114·12	3·5
38·04	2·0	123·63	3·4
47·55	3·0	133·14	3·1
57·06	3·1	142·65	3·0
66·57	3·5	152·16	3·0
76·08	3·5	161·67	3·0
89·59	3·75	171·18	3·0
95·10	4·00	180·69	3·0
104·61	3·75		

All experiments of a similar character with wires with a permanent torsion of 2, 3, 4, &c. showed that for a small magnetizing force the deflexion rose almost proportional to it, and that after a certain point further torsion was not produced by increasing the magnetizing force, and that ultimately with a greater magnetizing force the rod began very slightly to untwist.

8. The next experiment was made to discover any relationship which might exist between the initial torsion of the rod and that added to it by the force of the magnetic field when the magnetic force was constant. The following results were obtained. Up to some value of initial torsion between 10 and 15 the deflexion produced by magnetization is a maximum, and then it decreases as the torsion rises.

Initial Torsion.	Scale-divisions.	Initial Torsion.	Scale-divisions.
1	3·00	5	8·00
2	5·00	10	10·00
3	6·50	15	8·00
4	7·25		

By initial torsion I mean that the rod received a permanent torsional set of 1, 2, 3, &c. complete revolutions.

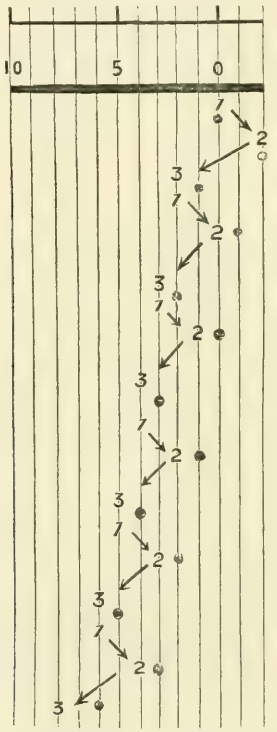
9. I noticed in the case of the last two values that after each magnetization the rod began to slowly untwist when the current was taken off. After each experiment the reading fell below the figure it started at. As an instance, the initial position was at 60 divisions; when the current was on, 69 was reached, and when the current was taken off the reading was 59.

Subsequent experiments showed that when a rod having permanent torsional set was used in induction experiments with a ballistic galvanometer, the induction followed in value the slow change of torsion of the rod. In some cases I noted the slow change from last February to the present time (July 30). Each induction experiment is modified by its predecessor having apparently changed the constitution of the rod.

10. In the next experiment this step by step unwinding of torsion after magnetization is shown in the case of a rod of nickel. The rod was placed in exactly the same position as the iron rod of the former experiments. The behaviour of nickel appears to be the same as that of iron, but in nickel the increase of torsion with magnetization is not so great. The twelve vertical lines, in the appended diagram, represent prolongations of the scale. In each case No. 1 indicates the position

of deflexion before the current is put on ; No. 2 the position of deflexion with current on ; No. 3 the new position to which the deflexion has come. This was the starting-point of the next deflexion. The magnetic force produced in all cases an increase of torsion in the direction of the initial torsion, so that in each case the amount of twisting in the direction of torsion was 2, and the untwisting about 1 in each set of magnetizations and demagnetizations. The wire did not untwist when left to itself, at least perceptibly in 100 minutes, but the untwisting after magnetization was immediate.

Fig. 1.



Step by Step Untwisting of Nickel.

11. Rods of non-magnetic metals (Cu, St, Pt, Pb, Ag, Zn, Cd, brass, and bronze) were subjected to the same treatment as the iron rods, but no rotation of any kind could be seen.

12. A rod of bismuth was next prepared by being drawn

into a glass tube when melted. If the glass tube be kept hot during the formation of the casting, and be cooled slowly, very long rods may be produced, in some cases 25 centim. long. The glass tube is removed from the metal by being cracked. When treated as the iron rods were in the previous experiments, no movement whatever could be perceived. From the brittle nature of Bi it could be subjected to only a slight amount of torsion.

13. A transitory current of electricity induced in a magnetic core subjected to *permanent torsional set*.

Fig. 2.

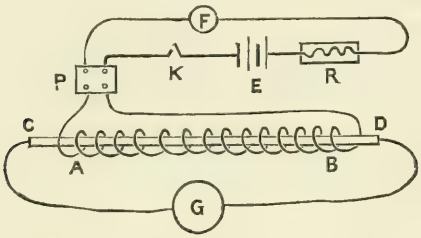


Diagram of Connexions, &c.

A B. A long helix of covered copper wire 30 centim. long, 2100 coils, mean area 0·5 centim.
C D. A rod of annealed iron 4 millim. diam., 30 centim. long.
G. Low-resistance galvanometer, astatic needles (constructed for ballistic work by Elliott).
P. Current-reverser.
K. Key.
E. Battery (2 E.P.S. accumulators).
R. A resistance-box.
F. Amperemeter.

The galvanometer was so placed that it was in no way affected, either by the helix A B or by the magnetic action of the core.

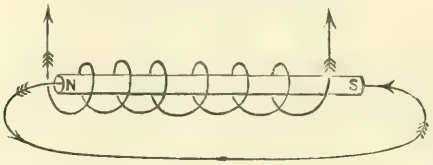
14. When the iron core C D was freshly annealed, and free from magnetization, except that produced by the inductive action of the earth's magnetizing force, a current was passed through the helix; a transient current was indicated by the galvanometer as existing in the circuit of which the iron core formed a part. The current produced a deflexion of 150 divisions of the scale; a Rowland inductor circle in the earth's horizontal field gave 300 divisions. (The log. of the

induction area of the Rowland coil = 4·97132 ; it has 42 turns, and a mean circumference 167·305 centim.) The value of the horizontal component of the earth field at Oxford at the time of these experiments was about 0·179 C.G.S. units. On breaking the circuit hardly any current was indicated, 1 or 1·5 divisions at the most. On again closing the circuit at K no current was indicated, and by repeating the closing no swing of the galvanometer-needle could be produced. The direction of the current was next changed by means of the commutator P. Then, on closing the circuit at K, a current of the same value as the former was indicated, but it was now in the opposite direction. On breaking or making the circuit no deflexion could be got from the iron core under examination.

So that in order to get a transient current from an iron core well annealed its magnetization must be reversed. An examination of cores under stress shows that the phenomenon may be modified.

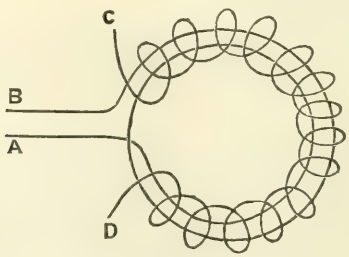
15. The relationship between the direction of the magnetizing current in the long helix and *iron core current* is shown in the diagram (fig. 3).

Fig. 3.



16. The experiment was next arranged so that the core might be as long as possible, and yet wound with a moderate length of copper helix. An iron core, A B, 6·3 metres long,

Fig. 4.



4 mm. diam., covered with a non-conducting coat, was coiled into a ring of about 15 centim. diam. It was next

coiled with a thick layer of swansdown cloth, and then with 600 turns of covered copper wire, so coiled as to have no lateral component. A, B were connected to the ballistic galvanometer, and C, D to the battery-circuit and K, &c. All the former effects were produced, but in a much greater degree, the deflexion of the galvanometer = 510 divisions. The magnetizing force due to the ring coil was so arranged as to be almost equal to that used in (14). A minute deflexion could be produced on either closing or opening the battery-circuit after the first effect.

17. An iron rod 1·5 millim. long, 1 centim. diam., was next coiled with a helix, and all the former effects were produced. The effect was not so marked as when bars of small diameter were used.

18. The remarkable feature of the phenomenon appears to be that it is only on the entire reversal of the magnetism of the core that the transient current is produced in any marked degree.

19. None of the effects could be got from brass or copper cores, so that the current from the iron core is due to the reversal of the magnetic matter of the core. In all the experiments, already described, the cores were as free from torsional stress as possible. Similar experiments were next made on cores which had a torsional set.

20. The marks ⟶ ⟵ in the appended tables indicate right-handed or left-handed torsion given to the core under examination (see Table I.). The torsion was given by fixing one end of the core and then rotating the other a certain number of times, and then deducting the number of turns in the opposite direction that the core took before settling down at its "set" torsional position. It was found that when the cores received 20 turns that they untwisted four turns, so that the whole torsion, at the condition of "set," was 16 turns. In all experiments tabulated, the marks † indicate an experiment made next after reversal of the current,

21. In these experiments, with cores subjected to torsional "set," the same markedly large deflexion of the needle of the galvanometer immediately after the reversal of the magnetizing current was clearly shown, but now only large *in one direction*, the direction depending on the direction of torsion of the core.

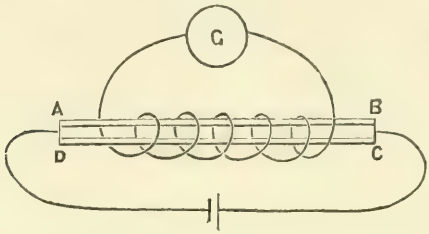
22. In Table I. the relationship existing between the direction of the magnetizing current, the *iron core current*, and the torsion of the core are shown.

In the next experiments (Table II.) the current was passed

through the iron core while the coil was in circuit with the galvanometer.

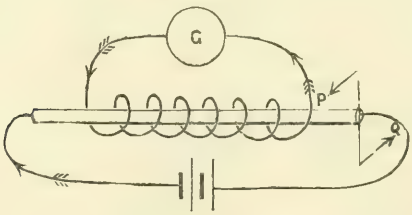
23. Two similar cores (fig. 5), having their sense of torsion opposite, but the amount of torsion in each equal, were put into the helix together, their ends A, D and B, C being joined to the battery-circuit; the current was passed through the cores, but no indication of current was manifested by the galvanometer G, the effect of one core apparently cancelling that of the other.

Fig. 5.



24. While a current was passing through the iron core subject to torsional set, a couple, indicated by the arrows P Q, was applied in the direction of the torsion of the core (fig. 6). When the arm O A was moved through 10°, suddenly a deflexion of 400 was given by the galvanometer. The length of the core was 50 centim., diam. 4 millim. The transient current was reversed by reversing the sense of the couple. When I made this experiment I had not read the work of

Fig. 6.

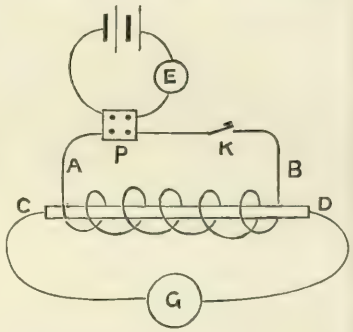


Wertheim, 1852. He produced the same effect in the same way—with an iron rod, but not under initial torsional set as was the case in my experiment.

Table I.

Results after the Core had received 16 ↺ turns.			Results after the Core had received 16 ↻ turns.		
No. of Experiment.	Direction of Current in Helix.	Deflexion of Galvanometer.	No. of Experiment.	Direction of Current in Helix.	Deflexion of Galvanometer.
1.....	A to B	10 L.	14.....	A to B	15 L.
2.....	† B „ A	60 L.	15.....	† B „ A	30 R.
3.....	B „ A	10 R.	16.....	B „ A	10 L.
4.....	† A „ B	35 R.	17.....	† A „ B	50 L.
5.....	A „ B	10 L.	18.....	A „ B	10 R.
6.....	A „ B	10 L.	19.....	A „ B	7 R.
7.....	A „ B	10 L.	20.....	A „ B	7 R.
8.....	† B „ A	35 L.	21.....	† B „ A	40 R.
9.....	B „ A	10 R.	22.....	B „ A	10 L.
10.....	B „ A	9 R.	23.....	B „ A	11 L.
11.....	† A „ B	34 R.	24.....	† A „ B	55 L.
12.....	A „ B	10 L.	25.....	A „ B	9 R.
13.....	A „ B	10 L.	26.....	A „ B	10 R.

Experiment I. (Plan of Connexion).



C D. Iron core.
G. Ballistic galvanometer.
A B. Magnetizing coil.
P. Reverser.
K. Key.
E. Amperemeter.

Two similar cores were prepared. one received 16 turns of torsion ↺ the other 16 ditto ↻.

Current through magnetizing helix.

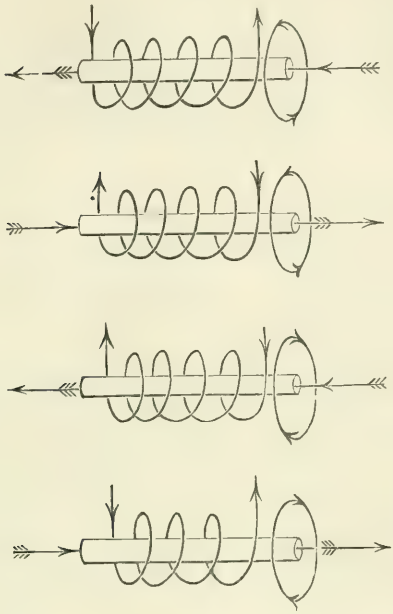
TABLE II.—Second Experiment. Current from the Battery sent through Iron Core.

No. of Experiment.	Direction of the Current in iron core with 16 turns.	Deflexion of Galvanometer.	No. of Experiment.	Direction of the Current in iron core with 16 turns.	Deflexion of Galvanometer.
1	A to B	90 L.	23	† A to B	185 R.
2	A „ B	20 L.	24	A „ B	40 R.
3	A „ B	20 L.	25	A „ B	40 R.
4	† B „ A	240 R.	26	† B „ A	120 L.
5	B „ A	40 R.	27	B „ A	8 L.
6	B „ A	30 R.	28	B „ A	7 L.
7	B „ A	25 R.	29	B „ A	5 L.
8	B „ A	20 R.	30	B „ A	0
9	B „ A	25 R.	31	B „ A	0
10	† A „ B	100 L.	32	† A „ B	153 R.
11	A „ B	0	33	A „ B	40 R.
12	A „ B	0	34	A „ B	35 R.
13	A „ B	0	35	A „ B	30 R.
14	A „ B	0	36	A „ B	30 R.
15	† B „ A	150 R.	37	† B „ A	136 L.
16	B „ A	25 R.	38	B „ A	10 L.
17	B „ A	25 R.	39	B „ A	10 L.
18	B „ A	23 R.	40	B „ A	10 L.
19	† A „ B	120 L.	41	† A „ B	155 R.
20	A „ B	0	42	A „ B	35 R.
21	A „ B	0	43	A „ B	30 R.
22	A „ B	0	44	A „ B	30 R.

The relationships which exist between the current in the iron core and transient current in the helix, and the current through the helix and the transient current in the iron core, the iron core being subject to torsion in the direction indicated, are shown by the four diagrams (fig. 7).

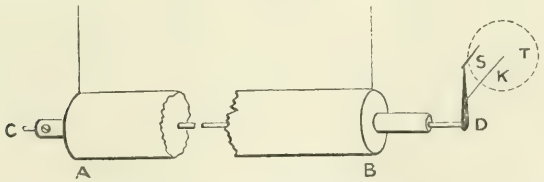
25. When the current which traversed the long solenoid, used in the first experiment, was interrupted by a tuning-fork driven electrically, an iron wire subject to torsional set, within the solenoid, gave out a loud musical note. It was shown by Page, long ago, that an iron rod within a solenoid, through which an interrupted current passed, would give out a musical note; but the note produced by a rod under torsional set in my experiment appears to be due to a cause somewhat different from that whereby Page's effect was produced. His note is said to be produced by minute elongations and shortenings of the rod. In the case of the rod being subject to torsion, as in the experiment now described, the note is evidently produced by torsional vibration, and that so great that, when a light pointer was fixed to the free end of the twisted rod, a record of its vibration was produced on the moving smoked-glass surface of the chronograph. I found no difficulty in making

Fig. 7.



it respond to 1000 vibrations per second, and record its movements clearly on the moving surface of the chronograph. The diagram (fig. 8) shows how the torsional magnetic stylus is constructed.

Fig. 8.



A B. The long solenoid, shown broken to save space.
C D. The twisted wire of iron.
S. An aluminium pointer, which is adjusted to touch the smoked glass plate of the chronograph.

Repeated tests show that the "latency" of this new form of stylus is exceedingly minute; this fact will, I believe, make the instrument very useful for getting accurate chronographic measurements.

26. I also found that when the stylus is connected, by means of a thread or fine wire, to a mica tympan T, true telephonic

effects could be obtained when a suitable transmitter is placed in the circuit, articulation being clear.

27. The very beautiful experiments of Prof. Hughes and of Prof. Ewing on transitory currents were made on wires in which torsional "set" had *not* been produced. In the experiments which have been described, rods with permanent torsional sets were always used, except in experiments (14) and (16).

L. *Notices respecting New Books.*

A Course of Experiments in Physical Measurement.—Part III. *Principles and Methods. By* Harold Whiting, *Ph.D.* Boston, U.S.A.: D. C. Heath and Co.

IN the two volumes of this work which have already appeared the author has described the processes used in the measurement of Physical Quantities, and has given full details concerning sources of error and the various methods of avoiding or eliminating them. Those parts of the theory of the subject upon which the experiments previously described are based are now briefly treated of in the book before us. The theory of errors also receives a very large share of attention, and in connexion with it is included the calculation of the mean from a series of observations, and the estimation of the probable error in the result.

The latter half of the volume consists of a collection of mathematical and physical tables, together with notes explaining their use. In the case of the tables of powers, roots, and reciprocals of numbers, and in one or two other cases also, two tables have been given; a rough one for all numbers of less than three digits, and a more complete one accurate to five figures. The former should prove useful for rapid work, and the latter for more refined calculations. We notice, however, that two tables are omitted which we have found to be of immense value in ordinary calculations, namely a table of four-figure logarithms and a corresponding one of antilogarithms. To be of maximum utility these should be placed in a conspicuous position, say at the end of the book, and should be so arranged that the whole of the logarithm table can be seen at one opening, and the same in the case of the antilogarithms. In our experience such tables are quite accurate enough for almost all calculations with the exception of delicate weighings on the balance, where the five-figure logarithms given by the author would be required. There is moreover a positive objection to the use of too elaborate mathematical tables, since they deceive the student into thinking that his results have the same order of accuracy as the tables.

The Physical Tables are fairly complete and accurate. The only error we have noticed is in the table of electromotive forces of cells, where the positive pole of the Clark cell is erroneously stated to be carbon instead of mercury. James L. Howard.

The Structure of the Sidereal Universe. By T. W. Backhouse, *F.R.A.S.* Demy 4to. Hills & Co., Sunderland.

No. 1 of the 'Publications of the West Hendon House Observatory, Sunderland,' by T. W. Backhouse, has just been issued, and gives the details on which the author's previous papers "On the Structure of the Sidereal Universe" (published in the 'Monthly Notices,' vol. i. p. 374, and in the 'Sidereal Messenger,' vol. ix. p. 337) were founded. The work is illustrated with figures and maps, and the numerous observations summarized in the text furnish a useful contribution to one of the grandest problems in astronomy. Mr. Backhouse's instruments are a 2-inch field-glass and a $4\frac{1}{4}$-inch refracting telescope, and he appears to have made excellent use of them. He remarks that certain large diffused nebulosities seen by Sir W. Herschel do not agree with those seen in a field-glass. This is not surprising when we reflect that Herschel used powerful appliances in his unwearying examination of the heavens. Mr. Backhouse says:—"We are brought to the conclusion that the galaxy is probably far nearer us than was at one time believed, and that therefore the greater part of the stars composing it are likely to be much smaller than the sun. The tendency of modern investigations is to diminish our ideas of the extent of the visible universe."

Astronomers will welcome further publications from the observatory at Sunderland. Private efforts of this laudable character are none too numerous in this country.

LI. *Intelligence and Miscellaneous Articles.*

RETINAL OSCILLATIONS. BY M. CHARPENTIER.

I HAVE recently investigated certain phenomena which, viewed as a whole, demonstrate experimentally the production of oscillations in the visual apparatus, when excited by light. These oscillations seem rather connected with a reaction of the retina, when it is acted on by light, than with the act of sensation itself. They are none the less interesting to know, and may serve as starting-point for a more minute analysis of the mechanism of the act in question.

The fact which led to these researches, and which I had communicated to the Société de Biologie on May 10, 1890, is the following:—If a black disk, on which is a larger or smaller white sector, is turned rather slowly, and if the centre of the disk is rigidly viewed when it is brightly illuminated, it is observed that that side of the white sector which first penetrates over the dark ground is bordered in its motion by a very sharp black band separated from the ground by a similar white band. These two bands appear in the form of sectors concentric with the disk, provided that certain necessary precautions are taken in the observation, in the detail of which I cannot enter here. The black band is shaded off at the edges; its angular extent, like that of the original white band, increases with the velocity of the disk, and in proportion to

it; but this extent expressed in time is always constant; the band takes always the same time to pass in front of a point of the retina; it commences about $\frac{1}{65}$ or $\frac{1}{70}$ after the passage of the white and lasts appreciably the same time. It is more visible the brighter the illumination of the white; but when it has been seen in these conditions it is found again easily under feebler illumination, in which it is only less striking. But this enfeeblement of the sensation, more or less marked according to the intensity of the excitation, is always observed.

It may be said that in this experiment there is spread out in space what occurs in time. The black band is in fact only a kind of reaction of the retina against the excitation by light, a reaction which may be made evident in a totally different way.

I have in fact observed that if in complete darkness we produce an instantaneous luminous excitation, or rather one of a duration which can be neglected in comparison with the first, the sensation appears *doubled*; that is to say, that when once it is formed it disappears, and again shows itself anew. This takes place, for instance, if we pass either through a Crookes or Geissler tube, or simply, but with less effect, through air, a *single* discharge from a Ruhmkorff coil. This doubling is more or less precise according to various circumstances which I have mentioned, but it is readily found again when it has once been observed: it is particularly marked with indirect vision. I have shown that it cannot be attributed to a reaction of the pupil, as I at first believed when I made my observations in a room not perfectly dark; it is in fact a retinal phenomenon.

There is then in this experiment, as in the first, a negative reaction under the influence of the excitation; the difference is that in the first case the excitation lasts when this reaction is seen, while here the excitation has come to an end, and only an obscuration of its persistent or consecutive image is seen.

Is this reaction, this negative excitation, unique? I do not think so: for in certain cases I have seen the dark band followed by other analogous bands uniformly spaced but much less distinct. The observation is moreover difficult, for a pretty great velocity of the disk is required, and then the bands, as they become larger, contrast less strongly with the ground, and become less perceptible. What is certain is that the first dark band is much less marked, and it dominates the phenomenon.

It would be difficult, and in any case premature, to indicate the causes of this appearance, but it may be permitted to characterize it as the result of a retinal oscillation formed under the influence of the start of the luminous excitation. What confirms this interpretation is that this oscillation travels along the retina with a uniform velocity from the point where it starts; and that by placing ourselves under certain experimental conditions we may, thanks to it, produce true phenomena of interference in the sensation.

The most convenient way of realizing these interferences is to turn a large black disk of about 0·4 metre with a velocity of about

one turn in a second, after having fixed on the periphery of this disk a very small white sector of 1° or 2°, and a height of 5 to 10 millim. In this way two necessary conditions are realized—a motion so rapid that there is a persistent image of this sector as extended as possible, and at the same time excitations at such intervals that the persistent images do not run into each other. If, then, the view is fixed rigidly towards a point at which the sector passes, which is the delicate and essential condition of the experiment, the persistent annular image of the object is seen to be channelled, and presents a certain number of dark zones regularly spaced out on the light ground. An intense light is not needed for this experiment.

The extent of the successive zones on the retina as well as their frequence is easily calculated.

It is found that the apparent interval between two dark zones on the disk diminishes with the distance from the eye. The image on the retina of this interval, on the contrary, remains constant.

For the same distance of the disk from the eye the interval in question varies with the velocity of the former, and, what is a point of capital importance, *inversely as this velocity*. This is not, then, a case of direct oscillations due to excitation, for they are, on the contrary, spaced out in proportion to the velocity of the disk.

This fact can only be explained by assuming that the object in moving over the retina is, in relation to the induced oscillation, in analogous conditions to those of an observer who moves away from a source of sound. If the retinal undulation which we have actually observed in the experiment with the black band travels with a constant velocity over the retina, the passage of a luminous image moving with a suitable rapidity should find this membrane in conditions periodically varying, in which the perception of the object will be alternately favoured or opposed. The distance of two neighbouring maxima and minima, which represents the apparent wave-length of this retinal undulation, should obey the relation expressed by Doppler's formula. This is what in fact is confirmed by experiment.—*Comptes Rendus*, July 20, 1891.

LECTURE-ILLUSTRATION OF COMPLEMENTARY COLOURS.

BY NIK. VON KLOBUKOW.

The method consists in dissolving the pigment-colours in suitable proportions in solvents which, differing considerably in specific gravity, are not soluble in each other, and neither of which dissolves the body in the other, and then, by violently shaking the solutions, and thus as it were effecting a mixture of the physical molecules, to bring about a mixture of colours.

The perception of colours is here brought about by direct action, as in the experiment of mixing colours by reflexion, and not, as in the colour-disk, by after-action of the luminous impression.

Owing to the above-mentioned properties of the solutions, the

liquids after being shaken together gradually separate, and the two layers of liquid are seen unchanged. By suitably changing the degree of dilution of the solutions, or by altering the proportions, any desired colour-effect can be easily obtained; on the other hand, by adding suitable materials to one or the other solution the duration of their mixture can be varied at will.

To exhibit the action of a mixture of *red* and *green* colouring-matters, aldehyde green in amylic alcohol is used for one solution and cobalt salt in water for the other. Of the various preparations of aldehyde green, the purest should be taken, which dissolves easily in amylic alcohol with a colour like that of solutions of nickel salts. It is not difficult just to hit the quantities in which the mixture appears of a dull white colour. Experiment shows that mixtures of pigments behave like mixtures of pure spectrum colours. Mixtures of cobalt and nickel solutions can also be used to demonstrate the action of complementary colours; by the addition of ammonium or sodium chloride, or other alkaline salts, to the solution of cobalt, the separation of the mixed liquids, which otherwise takes place slowly, can be accelerated at will. In order to get as pure a white as possible, the illumination must be as intense as practicable, and the experiment made in front of a dark background, care being taken to avoid any white objects.

To show the action of the mixture of *blue* and *yellow* colouring-matters, a solution of phenanthrenquinone in amylic alcohol may be used, which gives a yellow solution, and for blue a solution of ammonio-sulphate of copper.

For the mixture of *yellow* and *violet* the same solution can be used for the yellow, and a mixture of cobalt and copper salts in water for the violet, the tint being as near that of the spectrum as possible.—Wiedemann's *Annalen*, No. 6, 1891.

ON A REMARKABLE NEW ACID. BY TH. CURTIUS.

In the course of his researches on Hydrazine the author has obtained an extremely interesting body, *Azoimide*, or hydrogen-nitride, the composition of which corresponds to the formula

$$N_3H = \begin{matrix} N \diagdown \\ \| \\ N \diagup \end{matrix} \!\!> NH.$$

In the pure concentrated state it is a colourless liquid of extremely pungent odour, which boils at 37° without decomposition, and can be distilled, though it sometimes explodes with great violence at a much lower temperature. In an aqueous solution it behaves just as a halogen acid; like these it is monobasic, and forms salts with readiness. These salts, which are nitrides, correspond exactly to the chlorides. Nitrogen silver, Ag_3N, and the mercurous salt $(N_3)_2Hg_2$ explode when heated, or by a blow, with great violence. Nitrogen ammonium, $N_4H_4 = N_3(NH_4)$, is a body which crystallizes in large brilliant prisms, which can be sublimed without decomposition.—*Chemische Berichte*, vol. xxiii. p. 3023 (1890).

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

NOVEMBER 1891.

LII. *The Influence of Temperature on the Colour of Pigments*

By EDWARD L. NICHOLS *and* BENJAMIN W. SNOW *.

OUR knowledge of the laws which govern the changes of colour which many substances undergo when heated is very incomplete. Certain marked changes of colour which occur under the action of the blowpipe, and which are useful for the identification of the substance exhibiting them, have been noted and described, and some attempts have been made to show that these and other colour-changes follow a general law.

To Schœnbein† we owe the general observation that colours grow dark under the action of heat. E. J. Houston‡ (1871), working in association with Elihu Thomson, studied a great number of substances and noted their change of hue when heated. They stated their conclusion as follows:—". . . . the addition of heat causes the colour to pass from one of a greater to one of a less number of vibrations . . . ."

Ackroyd§ (1876), in a short but admirable paper, confirmed the observation of a movement of colour-tones "towards the red" upon heating. He supplemented naked-eye observations with spectroscopic study and reached the following result:—"That metachromatism arises from increased ab-

* Communicated by the Authors.

† Poggendorff's *Annalen*, xlv. p. 263.

‡ Journal of the Franklin Institute, 3rd series, lxii. p. 115.

§ "Metachromatism, or Colour Change," Chemical News, vol. xxxiv. p. 76.

sorption of light with elevation of temperature, the more refrangible increment increasing at a greater rate than the less refrangible." How accurate a statement of fact this is will appear when the measurements to be given in the present paper have been described.

The kindred topic of the influence of temperature upon absorption-spectra has claimed the attention of Gladstone*, Bartley†, and, very recently, of Conroy‡. Hitherto, however, there have been but few efforts to analyse systematically the selective reflexion which takes place at the surface of pigments§, and no attempts to trace out quantitatively those variations in the amount and character of the reflected light which are brought about by the action of heat.

It is our purpose in this paper to present the results of an investigation of the colour-changes which pigments undergo when subjected to wide ranges of temperature. The determinations included the spectroscopic analysis of the light from the pigment, with means of measuring its intensity, wave-length by wave-length, and the estimation of the temperature of the coloured surface.

The method of determining temperature which seemed to present the fewest objections, consisted in supporting a thin layer of the pigment on a ribbon of platinum foil, which could be maintained at any desired temperature by means of the electric current, and then measuring the linear expansion of the foil. To this end a strip, 25 centim. in length and 7 millim. wide, was cut from a sheet of platinum. The strip was placed in the circuit of a Gramme dynamo, and heated to a cherry-red. The degree of incandescence, which was observed to be in all parts the same, afforded a sufficient test of the uniformity of the foil. To the ends of this platinum strip were soldered brass rods, capable of carrying a heavy current without heating. These passed through the arms of a frame in which the strip was mounted, and one of them bore a compressed spiral spring, which served to keep the platinum ribbon properly stretched. By means of a dividing-engine two fine diamond rulings, 89 millim. apart, were drawn upon the foil at right angles to its length. Two microscopes, each

* Philosophical Magazine, [4] xiv. p. 423 (1857).
† Proceedings of the Royal Society, xxii. p. 241.
‡ Philosophical Magazine, [5] xxxi. p. 317 (1891).
§ With the exception of a few measurements made several years ago by one of us (Nichols, American Journal of Science, vol. xxviii. p. 343), the only quantitative study of the spectra of pigments with which we are acquainted is that contained in the recent paper of Abney and Festing on Colour Photometry (Phil. Trans. clxxix. p. 549).

provided with a micrometer eyepiece reading to 0·0025 millim., were now focused upon these lines, so that when the strip expanded longitudinally, under the heating action of the current, the increment could be readily and accurately measured.

The indications of this platinum thermometer enabled us to calculate the temperatures to which, from time to time, the foil and the film of pigment placed upon it were heated. In these computations we used Matthiessen's well-known formula, in which the length of a platinum wire is expressed as a function of its temperature. This formula,

$$l = l_0(1 + \cdot 00000851\,t + \cdot 0000000035\,t^2),$$

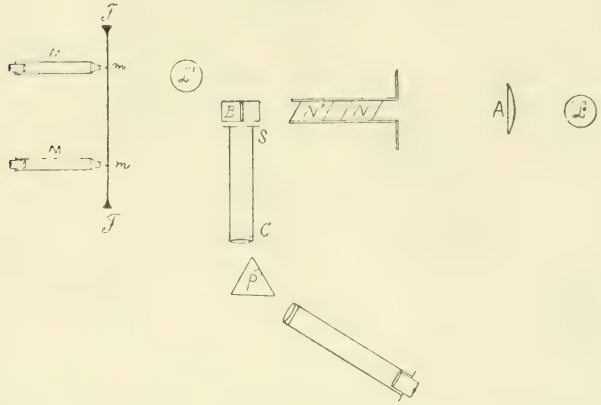
was originally determined between 0° and 100° C., and is strictly applicable only within that range. Beyond its proper interval it doubtless yields false values, and for very high temperatures the correction may be a considerable one. Although the correction-factor is at present unknown, the equation gives a convenient arbitrary scale of temperatures, which possesses the advantage of being readily reduced to the Centigrade system when the proper formula shall have been determined.

In the preparation of the film of pigment one of the two following methods was employed. In the case of the oxides of zinc and of magnesium the foil was smoked over the flame of the burning metal; in other cases the ribbon was well moistened with alcohol and the pigment was sifted upon it with a fine cloth, a quantity just sufficient to entirely conceal the metal being thus applied. Upon the evaporation of the alcohol there remained on the platinum a thin adherent layer, which possessed the natural surface of the dry powdered pigment, nearly free from gloss or surface-reflexion.

The instrument by means of which the photometric measurements were carried out was a form of polarizing spectrophotometer. The arrangement of its several essential parts, together with that of the apparatus used in connexion with it, is shown in the accompanying diagram (fig. 1). F F is the platinum strip, the mounting of which has already been described. To it were attached wires from a storage-battery of twenty cells, the amount of current, and consequently the temperature of the foil, being controlled by the variation of resistance in the circuit. The letters *m m* denote the positions of the diamond-lines; M M are the microscopes focused upon them for the measurement of temperature. The other side of the platinum foil, upon which the coating of colouring-matter is spread, is illuminated by an incandescent lamp, L′, which is supplied from another storage-battery. Light from this

lamp, diffusely reflected from the pigment, enters a rectangular prism at B, where it suffers total reflexion and is thrown

Fig. 1.

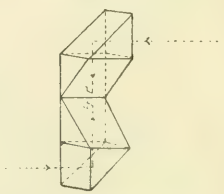


vertically downwards. The rays then enter another prism, identical in size and form with the first, which sends them through the upper half of the slit of the spectroscope in a direction parallel to the axis of the collimator-tube, S C.

In multiple circuit with the lamp L′, and supplied from the same battery, is the precisely similar lamp L, which serves as the reference standard. Rays from this lamp are first rendered parallel by the lens of short focus A, and then, before reaching the collimator, pass through the pair of Nicol prisms, N and N′, which act respectively as polarizer and analyser. The light upon emerging from the analyser enters a pair of reflecting prisms similar to those which have just been described and symmetrically placed, and so through the lower half of the slit into the collimator and along a path everywhere parallel to that followed by the light from the pigment.

The disposition of the four right-angled prisms before the slit is shown in fig. 2. This arrangement offers a certain advantage over the usual devices for introducing the rays of the comparison-light into the collimator-tube. The adjacent edges of the two inner prisms are in contact with the slit, and when viewed through the eyepiece they form a sharply defined boundary in the middle of the field. The result is that when two bundles of light are introduced by means of the device under con-

Fig. 2.



sideration, the spectra are separated by a much more clearly defined median line than can be secured with the ordinary comparison-prism at the slit. The sharpness of the inner boundary between the spectra to be compared has great influence upon the accuracy of the spectro-photometric determination; indeed, where close measurements are desired, definition in this region may be regarded as essential. There is another condition which is met by the use of the four prisms. The selective absorption of the glass through which the light passes in a spectro-photometer is by no means negligible. Even in the clearest of optical glass the absorption varies in a marked degree with the wave-length of the ray; and it is therefore important that the two sets of rays which are to furnish the spectra to be compared should be subjected to the same treatment, passing through the same or similar lenses and prisms and traversing the same total thickness of glass*. In the instrument used in our experiments this condition was fulfilled in every respect but one; viz. the light from the comparison-lamp L passed through the condensing-lens A and the two Nicol prisms which were not in the path of the rays from L′. The method by which the absorption due to these was eliminated will be indicated later.

After having traversed the collimator-tube, the rays from the pigment and those from the lamp L were dispersed by the prism p and passed on to the eyepiece. The field of view consisted of two spectra situated one above the other. By means of an adjustable diaphragm in the eyepiece any desired region of the spectrum could be isolated. When thus restricted the field consisted of two narrow vertical strips of colour, separated by a black line which was the image of the adjacent edges of the reflecting-prisms before the slit. The two strips of colour were identical in wave-length and differed only in intensity. The brightness of the lower depended upon that of the comparison-lamp L, and upon the angle between the polarizing-planes of the Nicol prisms. Of these last the polarizer N (fig. 1) had freedom of rotation, and was provided with a circle reading to five minutes of arc. The brightness of the upper field depended upon the amount of light, of the wave-length in question, reflected by the pigment under investigation. The spectrum of the comparison-lamp, although reduced by polarization, and by absorption and reflexion suffered in traversing the lens A and the calcite prisms, was

* Abney and Festing, in their paper on Colour Photometry, already cited, have pointed out the importance of this precaution (see p. 549 of their monograph).

still much the brighter of the two. The measurements consisted in turning the movable Nicol until the spectrum of lamp L was reduced, region for region, to equality with that of the spectrum due to the pigment.

In presenting the results of measurements with the spectrophotometer it is not always desirable to reduce the intensities to absolute measure, since it is with the luminosity rather than with the distribution of energy that we have to do. One of the most satisfactory ways of defining colour is to compare it with white as a standard, and that is the method which we have adopted for the purposes of this investigation. The ideal white is one which reflects all the wave-lengths of the visible spectrum in the same proportion. Whatever be the character of the illumination to which a body the colour of which is the ideal white is subjected, therefore, the incident and reflected rays will be identical in quality. Since no such body is known to exist, however, it becomes necessary to select some actual pigment as a reference-standard.

Dr. Arthur Kœnig, in one of his papers on colour-blindness, has suggested the adoption of magnesium oxide, obtained from the smoke of the burning metal, as the normal white *. Between this substance and magnesium carbonate, which one of the present writers has repeatedly used as a standard †, there is little to choose, so far as selective reflexion is concerned. Neither of them can be considered a true white, in the sense in which that term is to be understood in spectrophotometry ‡, but the oxide possesses two great advantages: the film is very readily produced, and the tint and the degree of brilliancy reappear in each new specimen with a constancy which leaves nothing to be desired. In our experiments, then, magnesium oxide was adopted as the reference-white, and the ideal white, in terms of the brightness of which all pigments were to be measured, was defined as a surface which, reflecting all wave-lengths of the visible spectrum equally well, possesses the same reflecting-power for the wave-length $\cdot 5890\,\mu$ (region of the D line) as does the smoke-film of magnesium oxide.

Our first step was to determine the correction-factor for the selective absorption suffered by the light from the lamp L, in traversing the lens A, and the Nicol prism. For this purpose a block of the carbonate of magnesium was cut in two. The

* Wiedemann's *Annalen*, xxii. p. 573.

† E. L. Nichols, American Journal of Science, xxviii. p. 343.

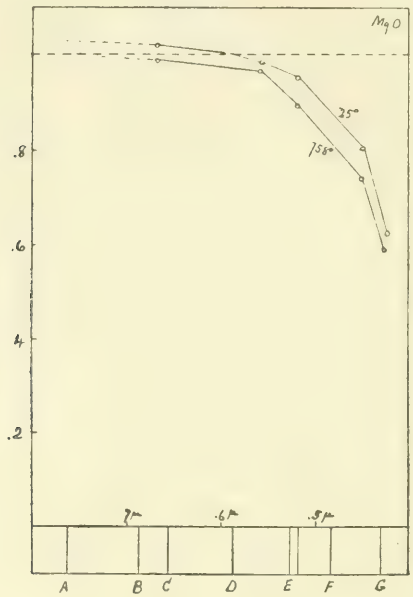
‡ E. L. Nichols, "On Black and White," Transactions of the Kansas Academy of Science, vol. x. p. 1 (1886).

new faces thus formed were rubbed together until they had acquired complete identity of surface-texure. One of the pieces was placed in the position usually occupied by the lamp L, the lamp itself being set up about ten centimetres away. The newly prepared surface was illuminated by the lamp, and it made an angle of 45 degrees with the axis of the polarizing prisms. The other piece of the carbonate was mounted in place of the platinum strip, and in the same manner as the first one. It was illuminated by rays from L′, which had been removed to a sufficient distance to restore the ratio of brightness of the two spectra to a convenient value. The spectra of the rays reflected by these two identical surfaces were compared, wave-length for wave-length, from red to violet. The difference, which was indeed most striking, could be due only to selective absorption by the condensing-lens and the Nicol prisms. Subsequent measurements, made when both pieces of magnesium carbonate were illuminated by the same lamp, showed that L and L′, which were lamps of the same type carefully adjusted to the same temperature, emitted the same quality of light, so that no correction for difference of illumination was necessary. It was not essential to our purpose to determine what portion of loss by absorption was due to the action of glass and what to calcite, but the effect of the two taken together was so surprisingly large that it seemed well worth while to separate them. This was readily accomplished by repeating the comparison of the spectra with the lens removed, a condition under which absorption within the calcite alone remained. The data obtained in these experiments upon the selective absorption in glass and calc-spar have no direct bearing upon the subject-matter of this paper. As they are in themselves of some interest, however, they will be communicated under a distinct title.

This preliminary investigation being completed and the correction-factors for absorption fixed upon, we proceeded to study the spectrum of magnesium oxide at 25° C. This was not one of the substances from which we expected marked effects as the result of heating, but we were anxious to determine in what manner it differed from true whiteness. The brightness of its spectrum in the region of the D-line, moreover, was the value to which all subsequent measurements were to be referred. Measurements were made at seven points in the visible spectrum, the wave-lengths of which are given in Table I. The brightness of each region is expressed in terms of that of the corresponding region in the spectrum

of the ideal white (already defined); a method which was followed in the case of all subsequent determinations. The results are shown graphically in fig. 3. In this diagram and in all that follow it, abscissæ are wave-lengths and ordinates are intensities. The spectrum of the normal white in each

Fig. 3.



case would be represented by a horizontal line, the ordinate of which is 1·00. It will be seen that the magnesium oxide differs from the ideal white in that it reflects the less refrangible rays more freely than it does those of shorter wave-length. The deficiency increases steadily towards the violet, where, in the region ·425μ, the pigment reflects only sixty-one one hundredths as much light as the ideal white would have done under the same illumination. The strip of foil, still bearing the smoke-film of magnesium oxide, was afterwards brought to 758° C., and the measurements were repeated with the pigment at that temperature. The values obtained (see Table I.) show a very slight decrease in reflecting-power but no change of colour.

TABLE I.—Reflecting-power of Magnesium Oxide at 25° and 758°, in terms of that of the ideal White.

Wave-lengths.	Temperature of the pigment:	
	25° C.	758° C.
μ.		
·7530		
·6685	1·021	0·988
·6080	0·994	
·5570	0·980	0·966
·5185	0·949	0·892
·4500	0·806	0·737
·4250	0·614	0·5843

First on our list of substances from which marked changes of colour under the action of heat might be looked for was sulphur. Every one is familiar with the increase in the intensity of the yellow hue when this substance is heated to temperatures in the neighbourhood of its melting-point. Our interest had been particularly aroused, however, by a statement of E. Wiedemann's to the effect that, when exposed to the intense cold obtained by contact with solid carbon dioxide, sulphur is not yellow, but white. Professor Wiedemann* alludes to this as to a well-known fact; but it was quite new to us, and we repeated the experiment, extending it to various other pigments, with results which will be described later.

For the purpose of the determination of the spectrum of sulphur, a layer of the powdered element was prepared by the method of moistening with alcohol, already described. When the film was dry, it was measured at 25° and at 103° C. The results are given in Table II. and in fig. 4.

TABLE II.—Reflecting-power of Sulphur at 25° and at 103°, in terms of that of the ideal White.

Wave-lengths.	Intensities at 25° C.	Intensities at 103° C.
μ.		
·6685	0·682	0·457
·6080	0·651	
·5570	0·634	0·368
·4920	0·571	0·332
·4685	0·318	0·205
·4500	0·163	0·094
·4340	0·055	0·040

The spectrum-curve of sulphur (fig. 4) is characteristic;

* *Beiblätter zu den Annalen der Physik*, xii. p. 791.

Fig. 4.

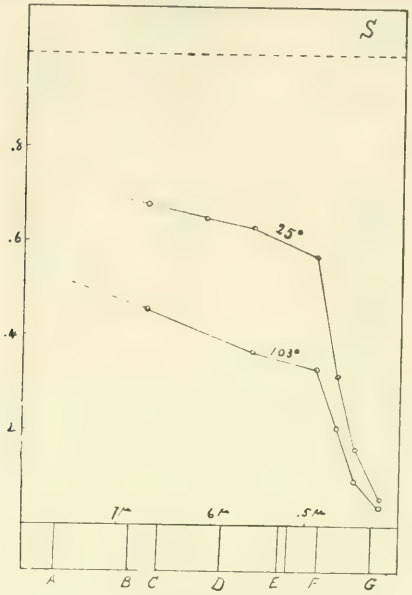


Fig. 5.

it cannot be mistaken for that of molybdic acid (fig. 5), of

massicot (fig. 6), of the yellow variety of mercuric iodide

Fig. 6.

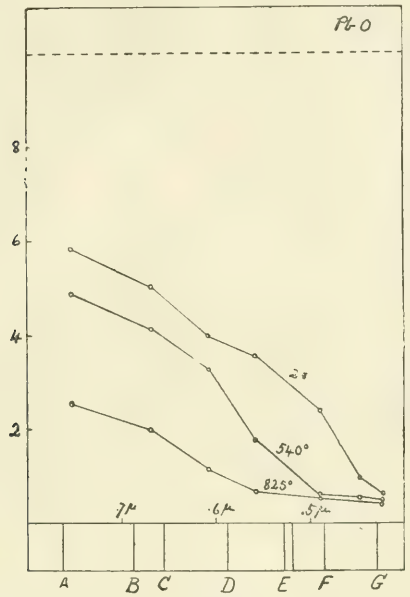
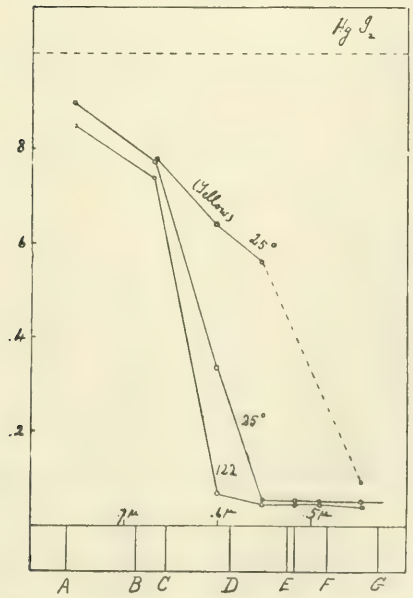


Fig. 7.



(fig. 7), or of lead chromate, the curve of which has

been given in one of the articles on colour already cited*.

All these substances show marked decrease of reflecting-power as we pass through the spectrum from red to violet. In the case of sulphur, the diminution is much less rapid than in other yellows until the region of the F line of Fraunhofer is reached. The curve then trends sharply downwards, indicating very rapid lessening of the reflecting-power towards the violet end of the spectrum.

The films of massicot and mercuric iodide were prepared as follows:—Coatings of red lead and of the red variety of mercuric iodide respectively were laid on in alcohol. When these were heated by the passage of the current, they were converted into the monoxide of lead (PbO) in the one and into the yellow form of the iodide in the other. The change took place spontaneously, when the requisite temperature was reached, without any disturbance of the film, and the colour of the pigment thus obtained was uniform and of uncommon brilliancy. The unstable yellow mercuric iodide, however, began to revert to the red form almost as soon as it became cold, and measurements were obtained in four regions only. The coating of molybdic acid was prepared by treatment with alcohol.

The results of our measurements of the spectra of these three substances are given in Tables III., IV., and V.

Table III.—Reflecting-power of Molybdic Acid in terms of that of the ideal White. Temperatures, 25° and 272° C.

Wave-lengths.	Intensities at 25° C.	Intensities at 272° C.
μ.		
·7530	.....	0·720
·6685	0·695	0·596
·6080	0·613	0·465
·5570	0·517	0·335
·4920	0·309	0·101
·4685	0·139	
·4500	0·068	0·040
·4340	0·045	

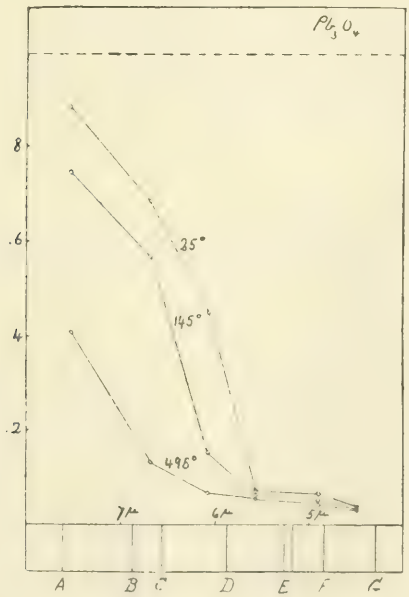
* See American Journal of Science, xxviii. p. 345.

TABLE IV.—Reflecting-power of Massicot (PbO) in terms of that of the ideal White. Temperatures, 25°, 540°, and 825° C.

Wave-lengths.	Intensities at 25° C.	Intensities at 540° C.	Intensities at 825° C.
μ.			
·7530	0·585	0·488	0·255
·6685	0·502	0·414	0·199
·6080	0·393	0·324	0·117
·5570	0·356	0·175	0·066
·4920	0·239	0·059	0·057
·4500	0·096	0·057	
·4250	0·060	.....	0·040

In addition to the results of measurements made upon the yellow iodide of mercury, Table V. contains data for the red variety at 25° and at 122°. The other red pigments subjected to investigation were :—Red lead (Table VI., fig. 8), sulphide

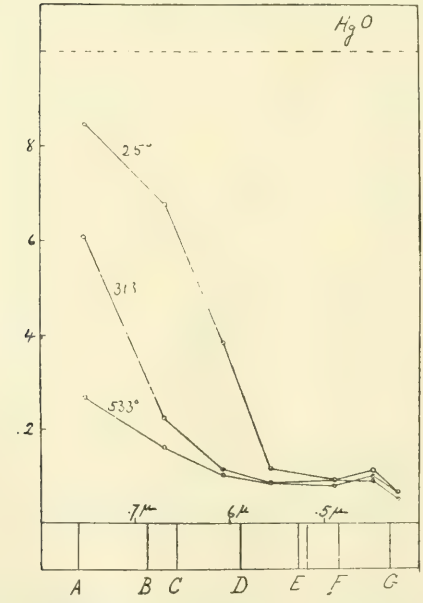
Fig. 8.



of mercury, Hg_2S (Table VII., fig. 9), and mercuric oxide,

Fig. 9.

Fig. 10.



HgO (Table VIII., fig. 10). A specimen of ferric oxide,

Fe_2O_3, which was measured at three temperatures (see Table IX., fig. 11), could not be properly classified as a red. It was the ordinary, well-known, rust-coloured powder.

Fig. 11.

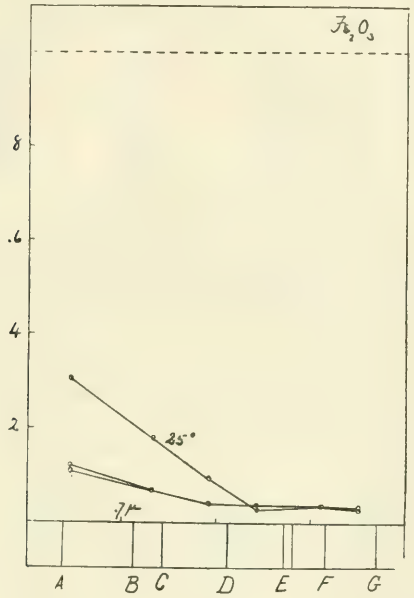


TABLE V.—Reflecting-power of Mercuric Iodide in terms of that of the ideal White. Temperatures, 25° and 122° C.

Wave-lengths.	Red Variety.		Yellow Variety.
	Intensities at 25° C.	Intensities at 122° C.	Intensities at 25° C.
μ.			
·7530	0·895	0·846	
·6689	0·771	0·744	0·776
·6080	0·330	0·066	0·635
·5570	0·050	0·046	0·561
·5185	0·058		
·4920	0·054	0·044	
·4500	0·055	0·032	0·091

TABLE VI.—Reflecting-power of Red Lead in terms of that of the ideal White.

Wave-lengths.	Intensities at 25° C.	Intensities at 145° C.	Intensities at 495° C.
μ.			
·7530	0·893	0·757	0·414
·6685	0·685	0·569	0·132
·6080	0·451	0·153	0·061
·5570	0·076	0·052	0·052
·4920	0·065	0·048	0·058
·4500	0·036	0·034	0·034

TABLE VII.—Reflecting-power of the Sulphide of Mercury (Hg_2S) in terms of that of the ideal White. Temperatures, 25° and 220° C.

Wave-lengths.	Intensities at 25° C.	Intensities at 220° C.
μ.		
·7530	0·853	0·333
·6685	0·710	0·237
·6370	0·465	0·059
·5820	0·038	0·021
·5570	0·030	
·4920	0·025	0·017
·4340	0·019	0·026

TABLE VIII.—Reflecting-power of Mercuric Oxide (HgO) in terms of that of the ideal White. Temperatures, 25°, 313°, and 523° C.

Wave-lengths.	Intensities at 25° C.	Intensities at 313° C.	Intensities at 523° C.
μ.			
·7530	0·849	0·612	0·266
·6685	0·678	0·221	0·161
·6080	0·381	0·112	0·104
·5570	0·119	0·083	0·082
·4920	0·093	0·080	0·093
·4685	0·093		
·4500	0·095	0·101	0·111
·4250	0·055	0·063	0·063

TABLE IX.—Reflecting-power of Ferric Oxide (Fe_2O_3) in terms of that of the ideal White. Temperatures, 25°, 493°, and 687° C.

Wave-lengths.	Intensities at 25° C.	Intensities at 493° C.	Intensities at 687° C.
μ.			
·7530	0·308	0·113	0·123
·6685	0·180	0·072	0·070
·6080	0·095	0·041	0·044
·5570	0·026	0·035	0·035
·4920	0·042	0·042	0·046
·4500	0·029	0·030	0·024

Our study of green and blue was a very cursory and incomplete one. It was confined indeed to the examination of chromic oxide and "artificial ultramarine." The former was of a very dull green colour. It was the usual preparation of the chemical laboratory, and not the more brilliant variety known as chrome-green.

On account of the very small amounts reflected by these pigments, the measurement of their spectra was attended with some difficulty. The results obtained, for which the same degree of accuracy as in the case of the foregoing determinations is not claimed, are given in Tables X. and XI. In the accompanying diagrams abscissæ are on the usual scale, but ordinates are increased five-fold.

It was evident to the unaided eye that the result of heating the ultramarine was to alter its hue permanently. A few measurements upon the cooled pigment were therefore made to determine the amount of the change. The results, which indicate very marked alteration in the colour of the substance, are given by themselves in Table XI.

TABLE X.—Reflecting-power of Chromic Oxide (Cr_2O_3) in in terms of that of the ideal White. Temperatures, 25°, 360°, and 730° C.

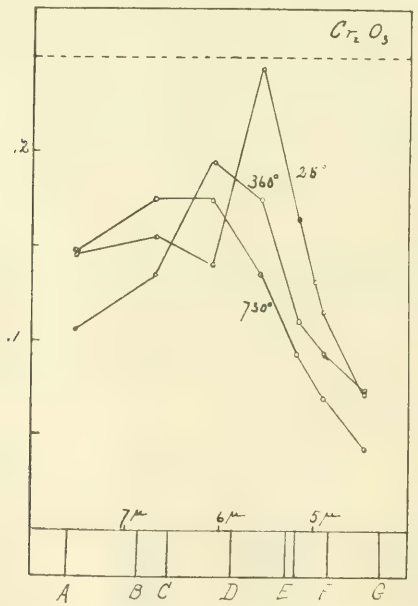
Wave-lengths.	Intensities at 25° C.	Intensities at 360° C.	Intensities at 730° C.
μ.			
·7530	0·058	0·042	0·059
·6685	0·062	0·054	0·070
·6080	0·056	0·078	0·070
·5570	0·098	0·069	0·054
·5185	0·073	0·044	0·037
·4920	0·046	0·038	0·028
·4500	0·029	0·032	0·017

TABLE XI.—Reflecting-power of Artificial Ultramarine in terms of that of the ideal White. Temperatures, 25°, 500°, and 773° C.

Wave-lengths.	Intensities at 25° C.	Intensities at 500° C.	Intensities at 773° C.	Intensities (after heating).
μ.				
·7530	0·028	0·027	0·037	0·027
·6685	0·026	0·021	0·042	0·021
·5570	0·012	0·017	0·021	0·021
·4920	0·081	0·042	0·038	0·080
·4685	0·195			
·4590	0·243			
·4500	0·224	0·057	0·048	0·124
·4410	0·232			
·4340	0·179			
·4290	0·145			
·4250	0·118	0·022	0·020	

The curves for chromic oxide (fig. 12) present a peculiarity

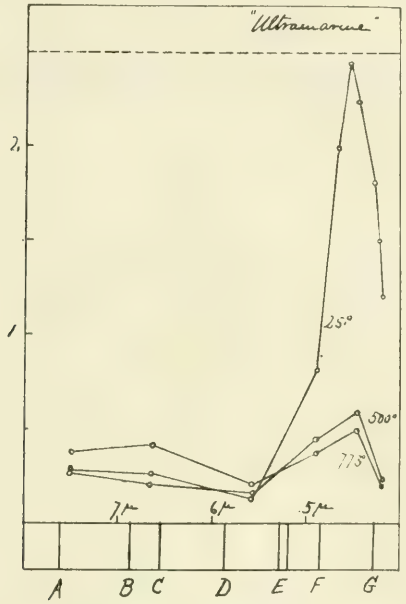
Fig. 12.



in the shifting of the maximum of reflecting-power from the green into the yellow, which is not met with in the case of any

of the other pigments studied. It is interesting to compare it in this respect with ultramarine (fig. 13), in which there

Fig. 13.



is a well-defined maximum in the blue, which is cut down in heating without any lateral displacement of the curve.

Both chromic oxide and ultramarine had been measured in the course of the earlier investigation on the spectrophotometry of pigments, to which reference has already been made. A comparison of the curves then published with those plotted from the data contained in Table XI. shows the ultramarine used in the original experiments to have been of very nearly the same brilliancy in the blue as the later specimen. The chromic oxide, however, was more than three times as bright in the green as that to which the quantities in Table XI. refer.

The series of experiments which have been described included also measurements of lamp-black, hot and cold, and of the oxide of zinc.

Our purpose in the study of lamp-black was simply to determine whether this substance, like the other pigments subjected to measurement, decreased in reflecting-power with rise of temperature, and if so, to what extent.

The changes in passing from 25° to 469° C. were found to be slight. Readings were made in three portions of the spectrum only, but in each of these the reflecting-power of the hot lamp-black is less than that of the cold. See Table XII.

TABLE XII.—Reflecting-power of Lamp-Black in terms of that of the ideal White. Temperatures, 25° and 469° C.

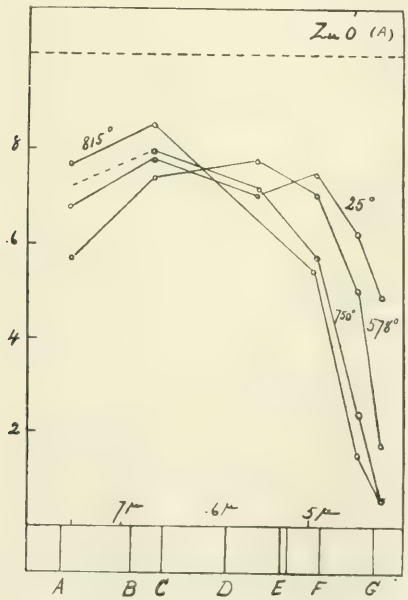
Wave-lengths.	Intensities at 25° C.	Intensities at 469° C.
μ.		
·6685	0·0055	0·0053
·5570	0·0072	0·0061
·4920	0·0073	0·0069

Zinc oxide was one of the pigments from which we expected to obtain very definite and well-marked results. The change of this substance from white to lemon-yellow, under the blowpipe, is one of the most familiar of colour-reactions. We anticipated no difficulty in fixing the precise nature of the changes which take place with rise of temperature. Films obtained by smoking the platinum foil over the flame of burning zinc were studied by the methods which already have been described in this paper. Our measurements yielded most erratic and, at first sight, inconsistent results. It soon became evident that in the study of the selective reflexion from zinc oxide at different temperatures we had to deal with a set of very complex phenomena; and it was indeed not until we had completed an investigation of the *radiation* of zinc oxide at high temperatures, a piece of work the results of which are to form the subject of another paper, that we were in position to understand the behaviour of that substance as regards reflecting-power. Our study of the radiation of the oxide at temperatures above the red heat showed the light emitted to be strongly selective, in the sense of differing greatly in distribution from that emanating from incandescent carbon or platinum at the same temperatures. It was found also that the character and intensity of the radiation were functions of time as well as of temperature. Every sharp fluctuation in radiating-power had its counterpart in colour-changes of the pigment, as viewed by reflected light, and the difficulty which we had experienced in measuring the pigment arose from the fact that we had to deal with a

luminescent surface of extremely evanescent and unstable character. At the time that our measurements of the reflecting-power were made, our knowledge of the conditions to be met was very incomplete. It is not possible by means of the data obtained to trace accurately the changes of colour which the oxide undergoes between ordinary temperatures and the red heat, to say nothing of the rapid time-changes which must take place at some of the higher temperatures. It is easy, however, to detect certain typical changes which the colour-curves undergo. The data given in Table XIII. have been selected with a view to illustrating these types.

The readings at 25°, 578°, 750°, and 815° were made with the same coating and in the order named. A set of measurements made at 884° have been discarded because they were to some extent vitiated by the presence of light directly radiated. An attempt was made to estimate the amount of such light and to apply a correction. The result was unsatisfactory. The four sets just mentioned have been plotted

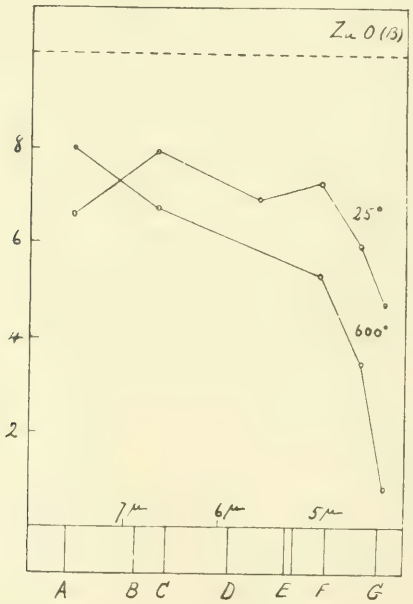
Fig. 14



together in fig. 14. The curves show, for the cold oxide, a spectrum weak both in the red and violet, with marked

indications of absorption between ·5μ and ·6μ. At high temperatures this absorption in the yellow disappears, and we see the gradual development of a maximum in the red. The case is of interest in that it is the only one in which reflecting-power at high temperatures exceeds that at lower temperatures for any considerable portion of the visible spectrum. The spectrum shown in fig. 14 is characteristic for zinc oxide at 25°, the same curves being obtained whenever a film was measured. The curves for high temperatures, however, were found to be applicable only to a single film, the variations being due to causes which we were not in a position to control. Another typical form is shown in fig. 15, in which the curve for 600° is that which characterizes a simple sulphur-yellow (compare with fig. 4). The curve for the cold film

Fig. 15.



in this case, however, differs in no essential from that which had been obtained from the film to which the previous figure pertains.

TABLE XIII.—Reflecting-power of Zinc Oxide in terms of that of the ideal White. Temperatures (A), 25°, 578°, 750°, and 815° C. (B) 25° and 600° C.

Wave-lengths.	(A) Intensities at				(B) Intensities at	
	25°.	578°.	750°.	815°.	25°.	600°.
μ.						
·7530	0·675	0·564	.....	0·769	0·654	0·797
·6685	0·779	0·734	0·793	0·854	0·794	0·685
·5570	0·705	0·759	0·712	0·650	0·691	0·587
·4920	0·749	0·707	0·569	0·549	0·727	0·532
·4500	0·620	0·501	0·238	0·150	0·598	0·347
·4250	0·486	0·178	0·049	0·049	0·470	0·076

In these experiments we investigated comparatively few of the long list of substances given by Houston and Thomson as subject to colour-change by heating, or of those catalogued by Ackroyd as "meta-chromic." A sufficient number were tested, however, to make it clear that colour-change by temperature is a very general phenomenon; also that the statements of Schœnbein, and of the later authors just mentioned, are accurate, in so far as their methods enabled them to observe the facts.

Our results may be summarized as follows:—

1. None of the pigments tested equals the ideal white in reflecting-power, even in that part of the spectrum for which its reflecting-power is greatest.

2. The reflexion spectrum of pigments arises from two distinct sources: (*a*) light reflected from the surface of the substance; (*b*) light reflected from interior faces. The light reflected from the surface is nearly white. Its brightness varies from about 2 per cent. (as in HgS) to nearly 10 per cent. (as in HgO). It is to the light internally reflected that the pigment owes its colour.

3. The effect of heating a pigment is invariably to diminish its reflecting-power, the diminution being as a rule more marked in regions of greatest refrangibility.

4. The changes of colour, observable when a pigment is heated, are due to this unequal loss of reflecting-power, and the effect which has been described as "a shifting of the colour towards the red," arises from the fact that the loss of brightness is least in the red and increases rapidly as we pass towards the violet end of the spectrum. There are cases,

however, like those of chromic oxide and the oxide of zinc, in which a shifting of a region of maximum of reflecting-power towards the longer wave-lengths actually occurs when the pigment is heated.

It had been our purpose in the investigation just described to extend our spectro-photometric measurements to the very low temperatures obtainable by the use of solid carbon dioxide, but we have been compelled by lack of time to content ourselves with noting such changes as could be detected with the unaided eye. The change observed was in every case that which would be brought about by increase of reflecting-power. There was no increase in the saturation of the colour, rather, on the other hand, a paling or dilution of the tint, as though there were a tendency towards white. Houston*, who made a similar set of observations at the higher temperatures reached by the evaporation of carbon bisulphide or sulphurous acid, arrived at a similar result. Ackroyd, from theoretical considerations, concluded that as the absolute zero is approached the prevailing tints of pigments will be blues and violets, merging finally into white.

Ackroyd, Hartley, as also Houston and Thomson, and still earlier Schœnbein and Brewster, have had something to say concerning the explanation of these phenomena. Their various views need not be touched upon here, unless it be to call attention to the opening paragraph of Ackroyd's paper, which contains an important statement. Ackroyd says :— "These changes embrace a class of phenomena, quite as important in their way as phosphorescence and fluorescence, *with which in fact they are intimately connected.*" It is our opinion that the connexion is indeed a most intimate one, and that every change of colour that pigments undergo is to be regarded simply as a symptom of changes in the radiating-power of the substance.

Physical Laboratory of Cornell University,
June 1891.

LIII. *Dynamical Problems in Illustration of the Theory of Gases.* *By* Lord Rayleigh, *Sec. R.S.*†

Introduction.

THE investigations, of which a part is here presented, had their origin in a conviction that the present rather unsatisfactory position of the Theory of Gases is due in some

* *Loc. cit.* p. 123.
† Communicated by the Author.

degree to a want of preparation in the mind of readers, who are confronted suddenly with ideas and processes of no ordinary difficulty. For myself, at any rate, I may confess that I have found great advantage from a more gradual method of attack, in which effort is concentrated upon one obstacle at a time. In order to bring out fundamental statistical questions, unencumbered with other difficulties, the motion is here limited to one dimension, and in addition one set of impinging bodies is supposed to be very small relatively to the other. The simplification thus obtained in some directions allows interesting extensions to be made in others. Thus we shall be able to follow the whole process by which the steady state is attained, when heavy masses originally at rest are subjected to bombardment by projectiles fired upon them indifferently from both sides. The case of pendulums, or masses moored to fixed points by elastic attachments, is also considered, and the stationary state attained under a one-sided or a two-sided bombardment is directly calculated.

Collision Formulæ.

If u', v' be the velocities before collision, u, v after collision, of two masses P, Q, we have by the equation of energy

$$\mathrm{P}(u'^2-u^2)+\mathrm{Q}(v'^2-v'^2)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and by the equation of momentum,

$$\mathrm{P}(u'-u)+\mathrm{Q}(v'-v)=0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From (1) and (2)

$$u'+u=v'+v, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or, as it may be written,

$$u'-v'=v-u,$$

signifying that the relative velocity of the two masses is reversed by the collision. From (2) and (3),

$$\left.\begin{aligned}(\mathrm{P}+\mathrm{Q})u'&=(\mathrm{P}-\mathrm{Q})u+2\mathrm{Q}v\\(\mathrm{P}+\mathrm{Q})v'&=2\mathrm{P}u+(\mathrm{Q}-\mathrm{P})v\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (4)$$

As is evident from (1) and (2), we may in (4), if we please, interchange the dashed and undashed letters. Thus from the first of (4),

$$(\mathrm{P}+\mathrm{Q})u=(\mathrm{P}-\mathrm{Q})u'+2\mathrm{Q}v',$$

or

$$u' = \frac{P+Q}{P-Q}u - \frac{2Q}{P-Q}v'$$

$$= u + \frac{2Q}{P-Q}(u-v'), \quad . \quad . \quad . \quad . \quad (5)$$

In the application which we are about to make, P will denote a relatively large mass, and Q will denote the relatively small mass of what for the sake of distinction we will call a projectile. All the projectiles are equal, and in the first instance will be supposed to move in the two directions with a given great velocity. After collision with a P the projectile rebounds and disappears from the field of view. Since in the present problem we have nothing to do with the velocity of rebound, it will be convenient to devote the undashed letter v to mean the given initial velocity of a projectile. Writing also q to denote the small ratio Q : P, we have

$$u' = u + \frac{2q}{1-q}(u-v). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If u and v be supposed positive, this represents the case of what we may call a favourable collision, in which the velocity of the heavy mass is increased. If the impact of the projectile be in the opposite direction, the velocity u'', which becomes u after the collision, is given by

$$u'' = u + \frac{2q}{1-q}(u+v). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The symbol v thus denotes the velocity of a projectile without regard to sign, and (7) represents the result of an unfavourable collision.

Permanent State of Free Masses under Bombardment.

The first problem that we shall attack relates to the *ultimate* effect upon a mass P of the bombardment of projectiles striking with velocity v, and moving indifferently in the two directions. It is evident of course that the ultimate state of a particular mass is indefinite, and that a definite result can relate only to probability or statistics. The statistical method of expression being the more convenient, we will suppose that a very large number of masses are undergoing bombardment independently, and inquire what we are to expect as the ultimate distribution of velocity among them. If the number of masses for which the velocity lies between u and $u+du$ be

denoted by $f(u)du$, the problem before us is the determination of the form of $f(u)$.

The number of masses, whose velocities lie between u and $u+du$, which undergo collision in a given small interval of time, is proportional in the first place to the number of the masses in question, that is to $f(u)\,du$, and in the second place to the relative velocity of the masses and of the projectiles. In all the cases which we shall have to consider v is greater than u, so that the chance of a favourable collision is always proportional to $v-u$, and that of an unfavourable collision to $v+u$. It is assumed that the chances of collision depend upon u in no other than the above specified ways. The number of masses whose velocities in a given small interval of time are passing, as the result of favourable collisions, from below u to above u, is thus proportional to

$$\int_{u'}^{u} f(w)\,.\,(v_1-w)\,dw, \quad . \quad . \quad . \quad . \quad . \quad (8)^*$$

where u' is defined by (6); and in like manner the number which pass in the same time from above u to below u, in consequence of unfavourable collisions, is

$$\int_{u}^{u''} f(w)\,.\,(v_1+w)dw, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

u'' being defined by (7). In the steady state as many must pass one way as the other, and hence the expressions (8) and (9) are to be equated. The result may be written in the form

$$v_1\left\{\int_{u'}^{u}-\int_{u}^{u''}\right\}f(w)dw=\int_{u'}^{u''}wf(w)dw. \quad . \quad . \quad (10)$$

Now, if q be small enough, one collision makes very little impression upon u; and the range of integration in (10) is narrow. We may therefore expand the function f by Taylor's theorem :—

$$f(w)=f(u)+(w-u)f'(u)+\tfrac{1}{2}(w-u)^2f''(u)+\ldots;$$

so that

$$\int f(w)dw=wf(u)+\tfrac{1}{2}(w-u)^2f'(u)+\tfrac{1}{6}(w-u)^3f''(u)+\ldots,$$

$$\left\{\int_{u'}^{u}-\int_{u}^{u''}\right\}f(w)dw=(2u-u'-u'')f(u)$$
$$-\tfrac{1}{2}\{(u'-u)^2+(u''-u)^2\}f'(u)+\ldots$$
$$=-\frac{4q}{1-q}uf(u)-\frac{4q^2}{(1-q)^2}(v^2+u^2)f'(u)+\text{cubes of } q. \quad (11)$$

* In the present problem $v_1=v$; but it will be convenient at this stage to maintain the distinction.

Also

$$\int wf(w)dw = \int \{(w-u)+u\} f(w)dw$$
$$= \tfrac{1}{2}(w-u)^2 f(u) + \tfrac{1}{3}(w-u)^3 f'(u) + \ldots$$
$$+ uf(u)\{wf(u) + \tfrac{1}{2}(w-u)^2 f'(u) + \ldots\};$$

so that

$$\int_{u'}^{u''} wf(w)dw = uf(u)\,.\,(u''-u')$$
$$+ \{\tfrac{1}{2}f(u) + \tfrac{1}{2}uf'(u)\}\{(u''-u)^2 - (u'-u)^2\} + \ldots$$
$$= \frac{4qv}{1-q}uf(u) + \frac{8q^2uv}{(1-q)^2}\{f(u) + uf'(u)\} + \text{cubes of } q. \quad (12)$$

As far as q^2 inclusive (10) thus becomes

$$\frac{4qv_1}{1-q}uf(u) + \frac{4q^2v_1}{(1-q)^2}(v^2+u^2)f'(u)$$
$$+ \frac{4qv}{1-q}uf(u) + \frac{8q^2uv}{(1-q)^2}\{f(u) + uf'(u)\} = 0,$$

or

$$uf(u)\{(1-q)v_1 + (1+q)v\} + qf'(u)\{v_1v^2 + u^2(v_1+2v)\} = 0.$$

If $v_1 = v$, q disappears from the first term as it stands, and will do so in any case in the limit when it is made infinitely small. Moreover, in the second term u^2 is to be neglected in comparison with v^2. We thus obtain

$$uf(u)\{1 + v/v_1\} + qv^2 f'(u) = 0 \quad . \quad . \quad . \quad (13)$$

as the differential equation applicable to the determination of $f(u)$ when q is infinitely small. The integral is

$$qv^2 \log f(u) + \tfrac{1}{2}(1 + v_1/v)u^2 = \text{constant},$$

or

$$f(u) = Ae^{-hu^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where

$$h = \frac{1 + v/v_1}{2qv^2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

or, if $v_1 = v$,

$$h = 1/qv^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The ultimate distribution of velocities among the masses is thus a function of the energy of the projectiles and not otherwise of their common mass and velocity. The ultimate state is of course also independent of the number of the projectiles.

The form of f is that found by Maxwell. To estimate the mean value of u^2 we must divide

$$\int_{-\infty}^{+\infty} u^2 f(u)\,du \text{ by } \int_{-\infty}^{+\infty} f(u)\,du.$$

Now

$$\int u^2 e^{-u^2/qv^2}du = -\tfrac{1}{2}qv^2\{ue^{-u^2/qv^2} - \int e^{-u^2/qv^2}du\},$$

so that

$$\int_{-\infty}^{+\infty} u^2 e^{-u^2/qv^2}du = \tfrac{1}{2}qv^2 \int_{-\infty}^{+\infty} e^{-u^2/qv^2}du.$$

The ratio in question is thus $\frac{1}{2}qv^2$, showing that the mean kinetic energy of a mass is *one half* that of a projectile, deviating from the law of equal energies first (1845) laid down by Waterston. We must remember, however, that we have thus far supposed the velocities of the projectiles to be all equal.

The value of A in (14) may be determined as usual. If N be the whole (very great) number of masses to which the statistics relate,

$$\mathrm{N} = \int_{-\infty}^{+\infty} f(u)\,du = \mathrm{A}\int_{-\infty}^{+\infty} e^{-u^2/qv^2}du = \mathrm{A}v\sqrt{(\pi q)};$$

so that

$$f(u)du = \frac{\mathrm{N}}{v\sqrt{(\pi q)}}\, e^{-u^2/qv^2}du. \quad . \quad . \quad . \quad (15')$$

If we were to suppose that the chances of a favourable or unfavourable collision were independent of the actual velocity of a mass, there would still be a stationary state defined by writing $v_1 = \infty$ in (15). Under these circumstances the mean energy would be twice as great as that calculated above.

It is easy to extend our result so as to apply to the case of projectiles whose velocities are distributed according to any given law $\mathrm{F}(v)$, of course upon the supposition that the projectiles of different velocities do not interfere with one another. We have merely to multiply by $\mathrm{F}(v)dv$ and to integrate between 0 and ∞. Thus from (13) we obtain

$$2uf(u)\int_0^{+\infty} v\mathrm{F}(v)\,dv + qf'(u)\int_0^{+\infty} v^3\mathrm{F}(v)\,dv = 0. \quad . \quad (17)$$

If $\mathrm{F}(v) = e^{-kv^2}$, we find

$$\int v^3 e^{-kv^2}dv = -\frac{1}{2k}\left\{v^2e^{-kv^2} - \int e^{-kv^2}2v\,dv\right\},$$

so that

$$\int_0^{+\infty} v^3 e^{-kv^2} dv = \frac{1}{k} \int_0^{+\infty} v e^{-kv^2} dv. \quad . \quad . \quad . \quad (18)$$

Our equation then becomes

$$2ku f(u) + q f'(u) = 0,$$

giving

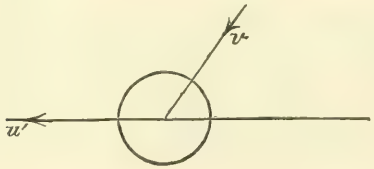
$$f(u) = \mathrm{A} e^{-ku^2/q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

The mean energy of the masses is $\frac{1}{2}q/k$, and this is now *equal* to the mean energy of the projectiles. We see that if the mean energy of the projectiles is given, their efficiency is greater when the velocity is distributed according to the Maxwell law than when it is uniform, and that in the former case the Waterston relation is satisfied, as was to be expected from investigations in the theory of gases.

It may perhaps be objected that the law e^{-kv^2} is inconsistent with our assumption that v is always great in comparison with u. Certainly there will be a few projectiles for which the assumption is violated; but it is pretty evident that in the limit when q is small enough, the effect of these will become negligible. Even when the velocity of the projectiles is constant, the law e^{-u^2/qv^2} must not be applied to values of u comparable with v.

The independence of the stationary state of conditions, which at first sight would seem likely to have an influence, may be illustrated by supposing that the motion of the masses is constrained to take place along a straight line, but that the direction of motion of the projectiles, striking always centrically, is inclined to this line at a constant angle θ.

If u' be the velocity of the mass (unity) before impact,



and u after impact, B the impulsive action between the mass and the projectile,

$$u - u' = \mathrm{B} \cos\theta.$$

Also, if v, V be the velocities of the projectile (q) before and after impact,

$$q(v - \mathrm{V}) = \mathrm{B};$$

so that

$$q(v-\mathrm{V})\cos\theta = u-u'.$$

By the equation of energy

$$u^2-u'^2 = q(v^2-\mathrm{V}^2).$$

From these we find, as before,

$$u' = u - \frac{2q\cos^2\theta}{1-q\cos^2\theta}\left(u-\frac{v}{\cos\theta}\right).$$

This may be regarded as a generalization of (6); and we see that it may be derived from (6) by writing $v/\cos\theta$ for v, and $q\cos^2\theta$ for q. In applying equation (10) to determine the stationary state, we must remember that the velocity of retreat is now no longer w, but $w\cos\theta$, so that (10) becomes

$$v\left\{\int_{u'}^{u} - \int_{u}^{u''}\right\} f(w)dw = \int_{w'}^{w''} w\cos\theta f(w)dw.$$

The entire effect of the obliquity θ is thus represented by the substitution of $v/\cos\theta$ for v, and of $q\cos^2\theta$ for q, and since these leave qv^2 unaltered, the stationary state, determined by (15), is the same as if $\theta=0$.

The results that we have obtained depend entirely upon the assumption that the individual projectiles are fired at random, and without distinction between one direction and the other. The significance of this may be illustrated by tracing the effect of a restriction. If we suppose that the projectiles are despatched in pairs of closely following components, we should expect that the effect would be the same as of a doubling of the mass. If, again, the components of a pair were so projected as to strike almost at the same time upon opposite sides, while yet the direction of the first was at random, we should expect the whole effect to become evanescent. These anticipations are confirmed by calculation.

By (5) the velocity u_1', which on collision becomes u, is

$$u_1' = \frac{1+q}{1-q}u \mp \frac{2q}{1-q}v;$$

so that the velocity, which after *two* consecutive collisions upon the same side becomes u, is given by

$$u_2' = \frac{1+q}{1-q}u_1 \mp \frac{2q}{1-q}v$$

$$= \frac{1+2q+(q^2)}{1-2q+(q^2)}u \mp \frac{4qv}{1-2q+(q^2)}.$$

The masses which by single collisions at velocity v would ultimately produce the same effect as these pairs are therefore very approximately $2q$.

If the projectiles be distributed in pairs in such a way that the components of each strike nearly simultaneously and upon *opposite* sides,

$$u_2' = \frac{1+q}{1-q}\left\{\frac{1+q}{1-q}u \pm \frac{2qv}{1-q}\right\} \mp \frac{2qv}{1-q}$$

$$= \frac{(1+q)^2}{(1-q)^2}u \pm \frac{4q^2v}{(1-q)^2}$$

$$= \frac{1+2q+(q^2)}{1-2q+(q^2)}u \pm \frac{4q\,.\,qv}{1-2q+(q^2)};$$

showing that the effect is the same as if the mass were doubled, and the velocity reduced from v to qv. Thus, when q is infinitely small, the effect is negligible in comparison with that obtained when the connexion of the components of a pair is dissolved, and each individual is projected at random.

Another Method of Investigation.

The method followed in the formation of equation (10) seems to lead most simply to the required determination of $f(u)$; but it is an instructive variation to consider directly the balance between the numbers of masses which change their velocities *from* and *to* u.

The number of masses whose velocities lie between u and $u+du$ being $f(u)du$, we have as the number whose velocities in a given small interval of time are expelled from the range du,

$$f(u)du(v-u) + f(u)\,du\,(v+u),$$

or

$$2vf(u)du.$$

This, in the steady state, is equal to the number which enter the range du from the two sides in consequence of favourable and unfavourable collisions; so that

$$f(u')(v-u')du' + f(u'')(v+u'')du'' - 2vf(u)du = 0\,. \qquad (20)$$

By (6), (7), since v is constant,

$$du' = \frac{1+q}{1-q}du, \quad du'' = \frac{1+q}{1-q}du\,;$$

so that

$$\frac{1+q}{1-q}f(u')\,.\,(v-u') + \frac{1+q}{1-q}f(u'')\,.\,(v+u'') - 2vf(u) = 0.$$

Now

$$v-u'=\frac{1+q}{1-q}(v-u),\ v+u''=\frac{1+q}{1-q}(v+u),$$

and thus

$$\frac{(1+q)^2}{(1-q)^2}\{(v-u)f(u')+(v+u)f(u'')\}-2vf(u)=0.$$

In this

$$f(u')=f(u)+\frac{2q(u-v)}{1-q}f'(u)+\frac{2q^2(u-v)^2}{(1-q)^2}f''(u)+\ldots$$

$$f(u'')=f(u)+\frac{2q(u+v)}{1-q}f'(u)+\frac{2q^2(u+v)^2}{(1-q)^2}f''(u)+\ldots;$$

so that

$$\frac{(1+q)^2}{(1-q)^2}\left\{2vf(u)+\frac{8qv}{1-q}uf'(u)+\frac{4q^2v^3}{(1-q)^2}f''(u)\right\}-2vf(u)=0,$$

or, when q is small enough,

$$8qv\{f(u)+uf'(u)\}+4q^2v^3f''(u)=0. \quad . \quad . \quad (21)$$

Accordingly

$$f(u)+uf'(u)+\tfrac{1}{2}qv^2f''(u)=0, \quad . \quad . \quad . \quad (22)$$

or on integration

$$uf(u)+\tfrac{1}{2}qv^2f'(u)=\mathrm{C}.$$

It is easy to recognize that the constant C of integration must vanish. On putting $u=0$, its value is seen to be

$$\mathrm{C}=\tfrac{1}{2}qv^2f'(0),$$

for $f(0)$ is not infinite. Now $f(u)$ is by its nature an even function of u, so that $f'(0)$ must vanish. We thus obtain the same equation (14) of the first order as by the former process.

Progress towards the Stationary State.

Passing from the consideration of the steady state, we will now suppose that the masses are initially at rest, and examine the manner in which they acquire velocity under the impact of the projectiles. In the very early stages of the process the momentum acquired during one collision is practically independent of the existing velocity (u) of a mass, and may be taken to be $\pm 2qv$. Moreover, the chance of a collision is at first sensibly independent of u. In the present investigation we are concerned not merely, as in considering the ultimate state, with the mass and velocity of a projectile, but also with the frequency of impact. We will denote by ν the whole number of projectiles launched in both directions

in the unit of time in the path of each mass. The chance of a collision for a given mass in time dt is thus represented by $\nu\,dt$. The number of collisions by which masses are expelled from the range du in time dt is $f(u)du\,.\,\nu\,dt$. The number which enter the range from the two sides is

$$\{f(u-2qv)+f(u+2qv)\}du\,.\,\tfrac{1}{2}\nu\,dt,$$

so that the excess of the number which enter the range over the number which leave is

$$\{\tfrac{1}{2}f(u-2qv)+\tfrac{1}{2}f(u+2qv)-f(u)\}du\,.\,\nu\,dt,$$

and this is to be equated to $\dfrac{df(u,t)du}{dt}\,dt$. Thus

$$\frac{df}{\nu\,dt}=\tfrac{1}{2}f(u-2qv)+\tfrac{1}{2}f(u+2qv)-f(u)=2q^2v^2\frac{d^2f}{du^2}, \quad (23)$$

the well-known equation of the conduction of heat. When $t=0$, $f(u)$ is to be zero for all finite values of u. The Fourier solution, applicable under these conditions, is

$$f(u,t')=\frac{\mathrm{A}}{\sqrt{t'}}e^{-u^2/4t'},$$

where t' is written for $2q^2v^2\nu t$. The total number of masses being N, we get to determine A

$$\mathrm{N}=\int_{-\infty}^{+\infty}f(u,t')du=2\sqrt{\pi}\,.\,\mathrm{A}\,;$$

so that

$$f(u,t')=\frac{\mathrm{N}}{2\sqrt{(\pi t')}}e^{-u^2/4t'}. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

If n be the whole number of collisions (for each mass), $n=\nu t$, and we have

$$4t'=4q^2v^2\,.\,2n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

If the unit of velocity be so chosen that the momentum $(2qv)$ communicated at each impact is unity, (24) takes the form

$$f(u,n)=\frac{\mathrm{N}}{\sqrt{(2\pi n)}}e^{-u^2/2n}, \quad . \quad . \quad . \quad . \quad (26)$$

which exhibits the distribution of momentum among the masses after n impacts. In this form the problem coincides with one formerly treated* relating to the composition of vibrations of arbitrary phases. It will be seen that there is a

* Phil. Mag. August 1880, p. 73

sharp contrast between the steady state and the early stages of the variable state. The latter depends upon the *momentum* of the projectiles, and upon the number of impacts; the former involves the *energy* of the projectiles, and is independent of the rapidity of the impacts.

The mean square of velocity after any number (n) of impacts is

$$N^{-1}\int_{-\infty}^{+\infty} u^2 f(u, n)du = n,$$

or, if we restore $4q^2v^2$,

$$\text{mean } u^2 = n \,.\, 4q^2v^2. \quad . \quad . \quad . \quad . \quad . \quad (27)$$

It must be distinctly understood that the solution expressed by (24), (25), (26) applies only to the first stages of the bombardment, beginning with the masses at rest. If the same state of things continued, the motion of the masses would increase without limit. But as time goes on, two causes intervene to prevent the accumulation of motion. When the velocity of the masses becomes sensible, the chance of an unfavourable collision increases at the expense of the favourable collisions, and this consideration alone would prevent the unlimited accumulation of motion, and lead to the ultimate establishment of a steady state. But another cause is also at work in the same direction, and, as may be seen from the argument which leads to (13), with equal efficiency. The favourable collisions, even when they occur, produce less effect than the unfavourable ones, as is shown by (6) and (7).

We will now investigate the general equation, applicable not merely to the initial and final, but to all stages of the acquirement of motion. As in (20), (23) we have

$$\frac{df(u,t)du}{dt}dt = \frac{\nu dt}{v}\{\tfrac{1}{2}f(u').(v-u')du' + \tfrac{1}{2}f(u'').(v+u'')du'' - f(u).v\,du\};$$

and thus by the same process as for (22)

$$\frac{df}{\nu\, dt} = 4q\frac{d}{du}\{uf(u)\} + 2q^2v^2\frac{d^2f}{du^2}. \quad . \quad . \quad . \quad (28)$$

If we write, as before,

$$t' = 2q^2v^2\nu t, \text{ and } h = 1/qv^2, \quad . \quad . \quad . \quad . \quad (29)$$

we have

$$\frac{df}{dt'} = \frac{d^2f}{du^2} + 2h\frac{d}{du}(uf). \quad . \quad . \quad . \quad . \quad (30)$$

Both in the case where the left side was omitted, and also when h vanished, we found that the solution was of the form

$$f = \surd\phi \,.\, e^{-\phi u^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where ϕ was constant, or a function of t' only. We shall find that the same form applies also to the more general solution. The factor $\surd\phi$ is evidently necessary in order to make $\int_{-\infty}^{+\infty} f(u)\,du$ independent of the time. By differentiation of (31),

$$\frac{df}{dt'} = \tfrac{1}{2}\phi_{-\frac{1}{2}} e^{-\phi u^2}(1-2\phi u^2)\frac{d\phi}{dt'},$$

$$\frac{d^2 f}{du^2} = -2\phi^{\frac{3}{2}} e^{-\phi u^2}(1-2\phi u^2),$$

$$u\frac{df}{du} + f = \phi^{\frac{1}{2}} e^{-\phi u^2}(1-2\phi u^2)\ ;$$

so that (30) is satisfied provided ϕ is so chosen as a function of t' that

$$\tfrac{1}{2}\phi^{-\frac{1}{2}}\frac{d\phi}{dt'} = -2\phi^{\frac{3}{2}} + 2h\phi^{\frac{1}{2}},$$

or

$$\frac{1}{4\phi^2}\frac{d\phi}{dt'} = -1 + \frac{h}{\phi}.$$

Thus

$$4t' = \int \frac{d\phi^{-1}}{1-h\phi^{-1}} = -\frac{1}{h}\log(1-h\phi^{-1}) + \text{const.},$$

where, however, the constant must vanish, since $\phi=\infty$ corresponds to $t'=0$. Accordingly

$$\phi = \frac{h}{1-e^{-4ht'}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

which with (31) completes the solution.

If t' is small, (32) gives $\phi = 1/4t'$, in agreement with (24); while if t' be great, we have $\phi = h = 1/qv^2$, as in (15′).

The above solution is adapted to the case where $f(u)=0$ for all finite values of u, when $t'=0$. The next step in the process of generalization will be to obtain a solution applicable to the initial concentration of $f(u)$, no longer merely at zero, but at any arbitrary value of u; that is, to the case where initially all the masses are moving with one constant velocity α.

Assume

$$f=\surd\phi\,.\,e^{-\phi(u-\psi)^2}, \quad . \quad . \quad . \quad . \quad . \quad (33)$$

where ϕ, ψ are functions of t' only. Substituting. as before, in (30), we find

$$\{1-2\phi(u-\psi)^2\}\left\{\tfrac{1}{2}\frac{d\phi}{dt'}+2\phi^2-2h\phi\right\}$$

$$+2\phi^2(u-\psi)\left\{\frac{d\psi}{dt}+2h\psi\right\}=0\,;$$

so that the equation is satisfied provided

$$\tfrac{1}{2}\frac{d\phi}{dt'}+2\phi^2-2h\phi=0, \quad . \quad . \quad . \quad . \quad . \quad (34)$$

and

$$\frac{d\psi}{dt'}+2h\psi=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

The first is the same equation as we found before, and its solution is given by (32); while (35) gives

$$\psi=\alpha e^{-2ht'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Thus (32), (33), (36) constitute the complete solution of the problem proposed, and show how the initial concentration at $u=\alpha$ passes gradually into the steady state when $t'=\infty$. In the early stages of the process.

$$f(u,t')=\frac{1}{\surd(4t')}\,e^{-(u-\alpha)^2/4t'}; \quad . \quad . \quad . \quad . \quad (37)$$

to which the factor $N/\surd\pi$ may be applied, when it is desired to represent that the whole number of masses is N. It appears that during the whole process the law of distribution is in a sense maintained, the only changes being in the value of u round which the grouping takes place, and in the degree of concentration about that value.

There will now be no difficulty in framing the expression applicable to an arbitrary initial distribution of velocity among the masses. For this purpose we need only multiply (33) by $\chi(\alpha)\,d\alpha$, and integrate over the necessary range. Thus

$$f(u,t')=\surd\phi\,.\int_{-\infty}^{+\infty}d\alpha\,\chi(\alpha)\;Exp\{-\phi(u-\alpha e^{-2ht'})^2\}, \quad . \quad (38)$$

ϕ being given, as usual, by (32). The limits for α are taken $\pm\infty$; but we must not forget that the restriction upon the magnitude of u requires that $\chi(u)$ shall be sensible only for values of u small in comparison with v.

When is small, we have from (38),

$$f(u,t') = \frac{1}{\sqrt{(4t')}} \int_{-\infty}^{+\infty} d\alpha\, \chi(\alpha)\, e^{-(u-\alpha)^2/4t'} = \sqrt{\pi}\,.\,\chi(u) \text{ ultimately};$$

so that

$$\chi(\alpha) = \frac{1}{\sqrt{\pi}} f(\alpha, 0).$$

Accordingly the required solution expressing the distribution of velocity at t' in terms of that which obtains when $t'=0$, is

$$f(u,t') = \sqrt{\frac{\phi}{\pi}} \cdot \int_{-\infty}^{+\infty} d\alpha f(\alpha, 0)\, \mathrm{Exp}\{-\phi(u-\alpha e^{-2ht'})^2\} \ldots (39)$$

We may verify this by supposing that $f(u,0) = e^{-hu^2}$, representing the steady state. The integration of (39) then shows that

$$f(u,t') = e^{-hu^2},$$

as of course should be.

An example of more interest is obtained by supposing that initially

$$f(u,0) = e^{-h'u^2}; \quad \ldots \ldots \quad (40)$$

that is, that the velocities are in the state which would be a steady state under the action of projectiles moving with an energy different from the actual energy. In this case we find from (32), (39),

$$f(u,t') = \sqrt{\left(\frac{\phi}{\phi - h + h'}\right)}\, e^{-\frac{\phi h' u^2}{\phi - h + h'}}. \quad \ldots (41)$$

We will now introduce the consideration of variable velocity of projectiles into the problem of the progressive state. In (28) we must regard ν as a function of v. If we use $\nu\, dv$ to denote the number of projectiles launched in unit of time with velocities included between v and $v+dv$, (28) may be written

$$\frac{df}{dt} = 4q \int \nu\, dv\,.\,\frac{d}{du}\{uf(u)\} + 2q^2 \int \nu\, v^2\, dv\,.\,\frac{d^2 f}{du^2}, \quad \ldots (42)$$

which is of the same form as before. The only difference is that we now have in place of (29),

$$t' = 2q^2 t \int \nu\, v^2\, dv, \quad \ldots \ldots \quad (43)$$

$$h = \int \nu\, dv \div q \int \nu\, v^2\, dv. \quad \ldots \ldots \quad (44)$$

In applying these results to particular problems, there is an important distinction to be observed. By definition $\nu\, dv$ represents the number of projectiles which in the unit *time*

pass a given place with velocities included within the prescribed range. It will therefore not represent the distribution of velocities in a given *space*; for the projectiles, passing in unit time, which move with the higher velocities cover correspondingly greater spaces. If therefore we wish to investigate the effect of a Maxwellian distribution of velocities among the projectiles, we are to take, not $\nu = Be^{-kv^2}$, but

$$\nu = B\, v\, e^{-kv^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

In this case, by (18),

$$h = k/q\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

and, as we saw, the mean energy of a mass in the steady state is equal to the mean energy of the projectiles which at any moment of time occupy a given space. From (43),

$$t' = Bq^2k^{-2}t. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

Pendulums in place of Free Masses.

We will now introduce a new element into the question by supposing that the masses are no longer free to wander indefinitely, but are moored to fixed points by similar elastic attachments. And for the moment we will assume that the stationary state is such that no change would occur in it were the bombardment at any time suspended. To satisfy this condition it is requisite that the phases of vibrations of a given amplitude should have a certain distribution, dependent upon the law of force. For example, in the simplest case of a force proportional to displacement, where the velocity u is connected with the amplitude (of velocity) r and with the phase θ by the relation $u = r\cos\theta$, the distribution must be uniform with respect to θ, so that the number of vibrations in phases between θ and $\theta + d\theta$ must be $d\theta/2\pi$ of the whole number whose amplitude is r. Thus if r be given, the proportional number with velocities between u and $u + du$ is

$$\frac{du}{2\pi\sqrt{(r^2 - u^2)}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

And, in general, if r be some quantity by which the amplitude is measured, the proportional number will be of the form

$$\phi(r, u)\, du, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

where ϕ is a determinate function of r and u, dependent upon the law of vibration. If now $\chi(r)\, dr$ denote the number of vibrations for which r lies between r and $r + dr$, we have altogether for the distribution of velocities u,

$$f(u) = \int \chi(r)\, \phi(r, u)\, dr. \quad . \quad . \quad . \quad . \quad (50)$$

If the vibrators were left to themselves, $\chi(r)$ might be chosen arbitrarily, and yet the distribution of velocity, denoted by $f(u)$, would be permanent. But if the vibrators are subject to bombardment, $f(u)$ cannot be permanent, unless it be of the form already determined. The problem of the permanent state may thus be considered to be the determination of $\chi(r)$ in (50), so as to make $f(u)$ equal to e^{-hu^2}.

We will now limit ourselves to a law of force proportional to displacement, so that the vibrations are isochronous; and examine what must be the form of $\chi(r)$ in (8) in order that the requirements of the case may be satisfied.

By (15′), if N be the whole number of vibrators,

$$\frac{N\sqrt{h}}{\sqrt{\pi}}\,e^{-hu^2}=\int_u^\infty \frac{\chi(r)\,dr}{2\pi\sqrt{(r^2-u^2)}}. \quad . \quad . \quad . \quad (51)$$

The determination of the form of χ is analogous to a well-known investigation in the theory of gases. We assume

$$\chi(r)=Ar\,e^{-hr^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

where A is a constant to be determined. To integrate the right-hand member of (51), we write

$$r^2=u^2+\eta^2; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

so that

$$\int_u^\infty \frac{\chi(r)\,dr}{\sqrt{(r^2-u^2)}}=A\int_0^\infty e^{-h(u^2+\eta^2)}\,d\eta=\frac{A\sqrt{\pi}}{2\sqrt{h}}\,e^{-hu^2}.$$

Thus

$$A=4hN. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

The distribution of the amplitudes (of velocity) is therefore such that the number of amplitudes between r and $r+dr$ is

$$N\,.\,4hr\,e^{-hr^2}\,dr, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

while for each amplitude the phases are uniformly distributed round the complete cycle.

The argument in the preceding paragraphs depends upon the assumption that a steady state exists, which would not be disturbed by a suspension, or relaxation, of the bombardment. Now this is a point which demands closer examination; because it is conceivable that there may be a steady state, permanent so long as the bombardment itself is steady, but liable to alteration when the rate of bombardment is increased or diminished. And in this case we could not argue, as before, that the distribution must be uniform with respect to θ.

If x denote the displacement of a vibrator at time t,

$$x=n^{-1}\,r\sin(n\,t-\theta), \quad dx/dt=r\cos(nt-\theta).$$

When $t=0$,

$$x=-n^{-1}r\sin\theta, \quad dx/dt=u=r\cos\theta;$$

and we may regard the amplitude and phase of the vibrator as determined by u, η, where

$$u=r\cos\theta, \quad \eta=r\sin\theta.$$

Any distribution of amplitudes and phases may thus be expressed by $f(u, \eta)\, du\, d\eta$.

If we consider the effect of the collisions which may occur at $t=0$, we see that u is altered according to the laws already laid down, while η *remains unchanged.* The condition that the distribution remains undisturbed by the collisions is, as before, that, for every constant η, $f(u, \eta)$ should be of the form e^{-hu^2}, or, as we may write it,

$$f(u, \eta)=\chi(\eta)\, e^{-hu^2}.$$

But this condition is not sufficient to secure a stationary state, because, even in the absence of collisions, a variation would occur, unless $f(u, \eta)$ were a function of r, independent of θ. Both conditions are satisfied, if $\chi(\eta)=\mathrm{A}\, e^{-h\eta^2}$, where A is a constant; so that

$$f(u, \eta)\, du\, d\eta=\mathrm{A}\, e^{-h(u^2+\eta^2)}\, du\, d\eta=2\pi\mathrm{A}\, e^{-hr^2}\, r\, dr.$$

Under this law of distribution there is no change either from the progress of the vibrations themselves, or as the result of collisions.

The principle that the distribution of velocities in the stationary state is the same as if the masses were free is of great importance, and leads to results that may at first appear strange. Thus the mean kinetic energies of the masses is the same in the two cases, although in the one case there is an accompaniment of potential energy, while in the other there is none. But it is to be observed that nothing is here said as to the rate of progress towards the stationary condition when, for instance, the masses start from rest; and the fact that the ultimate distribution of velocities should be independent of the potential energy is perhaps no more difficult to admit than its independence of the number of projectiles which strike in a given time. One difference may, however, be alluded to in passing. In the case of the vibrators it is necessary to suppose that the collisions are instantaneous; while the result for the free masses is independent of such a limitation.

The simplicity of f in the stationary state has its origin in the independence of θ. It is not difficult to prove that this

law of independence fails during the development of the vibrations from a state of rest under a vigorous bombardment. The investigation of this matter is accordingly more complicated than in the case of the free masses, and I do not propose here to enter upon it.

In a modification of the original problem of some interest even the stationary distribution is not entirely independent of phase. I refer to the case where the bombardment is from one side only, or (more generally) is less vigorous on one side than on the other. It is easy to see that a one-sided bombardment would of necessity disturb a uniform distribution of phase, even if it were already established. The permanent state is accordingly one of unequal phase-distribution, and is not, as for the symmetrical bombardment, independent of the vigour with which the bombardment is conducted.

But in one important particular case the simplicity of the symmetrical bombardment is recovered. For if the number of projectiles striking in a given time be sufficiently reduced, the stationary condition must ultimately become one of uniform phase-distribution.

Under this limitation it is easy to see what the stationary state must be. Since the ultimate distribution is uniform with respect to phase, it must be the same from whichever side the bombardment comes. Under these circumstances it could not be altered if the bombardment proceeded indifferently from both sides, which is the case already investigated. We conclude that, *provided the bombardment be very feeble*, there is a definite stationary condition, independent both of the amount of the bombardment and of its distribution between the two directions. It is of course understood that from whichever side a projectile be fired, the moment of firing is absolutely without relation to the phase of the vibrator which it is to strike.

The problem of the one-sided bombardment may also be attacked by a direct calculation of the distribution of amplitude in the stationary condition. The first step is to estimate the effect upon the amplitude of a given collision. From (6), if u' be the velocity before collision, and u after,

$$u = u' + \frac{2q}{1+q}(v-u').$$

The fraction $2q/(1+q)$ occurs as a whole, and we might retain it throughout. But inasmuch as in the final result

only one power of q need be retained, it will conduce to brevity to omit the denominator at once, and take simply

$$u = u' + 2q(v - u'). \quad . \quad . \quad . \quad . \quad . \quad (56)$$

Thus if ρ, ϕ and r, θ be the amplitude and phase before and after collision respectively,

$$\left.\begin{aligned} r\cos\theta &= \rho\cos\phi + 2q(v - \rho\cos\phi), \\ r\sin\theta &= \rho\sin\phi\ ; \end{aligned}\right\} \quad . \quad . \quad (57)$$

so that

$$r^2 = \rho^2 + 4q\rho\cos\phi\ (v - \rho\cos\phi) + 4q^2(v - \rho\cos\phi)^2.$$

From this we require the approximate value of ρ in terms of r and ϕ. The term in q^2 cannot be altogether neglected, but it need only be retained when multiplied by v^2. The result is

$$\rho = r - \delta r,$$

where

$$\delta r = 2q(v\cos\phi - r\cos^2\phi) + \frac{2q^2v^2}{r}\sin^2\phi. \quad . \quad (58)$$

This equation determines for a given ϕ the value of ρ which the blow converts into r. Values of ρ nearer to r will be projected across that value. The chance of a collision at ρ, ϕ is proportional to $(v - \rho\cos\phi)$. Thus if a number of vibrators in state ρ, ϕ be $\mathrm{F}(\rho)\, d\rho\, d\phi$*, the condition for the stationary state is

$$\int_0^{2\pi} d\phi \int_\rho^r (v - \rho\cos\theta)\, \mathrm{F}(\rho)\, d\rho = 0, \quad . \quad . \quad . \quad (59)$$

the integral on the left expressing the whole number (estimated algebraically) of amplitudes which in a small interval of time pass outwards through the value r.

By expansion of $\mathrm{F}(\rho)$ in the series

$$\mathrm{F}(\rho) = \mathrm{F}(r) + \mathrm{F}'(r)\,(\rho - r) + \ldots,$$

we find

$$\int_\rho^r \mathrm{F}(\rho)\, d\rho = \mathrm{F}(r)\, \delta r - \tfrac{1}{2}\, \mathrm{F}'(r)\, (\delta r)^2 + \text{cubes of } q,$$

$$\int_\rho^r \rho\, \mathrm{F}(\rho)\, d\rho = r\, \mathrm{F}(r)\, \delta r - \tfrac{1}{2}\, (\delta r)^2 \{\mathrm{F}(r) + r\mathrm{F}'(r)\} + \text{cubes of } q.$$

* We here assume that the bombardment is feeble.

Again from (58),

$$\int_0^{2\pi} \delta r \, d\phi = -qr + q^2v^2/r,$$

$$\int_0^{2\pi} \cos\phi \, \delta r \, d\phi = qv,$$

$$\int_0^{2\pi} (\delta r)^2 \, d\phi = 2q^2v^2,$$

$$\int_0^{2\pi} \cos\phi \, (\delta r)^2 \, d\phi = 0.$$

The condition for the stationary state is therefore

$$v\{\mathrm{F}(r)\,(-qr+q^2v^2/r) - \mathrm{F}'(r)\,q^2v^2\} - r\,\mathrm{F}(r)\,qv = 0,$$

or

$$\mathrm{F}(r)\{-2r+qv^2/r\} - \mathrm{F}'(r)\,qv^2 = 0.$$

Thus, on integration,

$$r^2 - qv^2 \log r + qv^2 \log \mathrm{F}(r) = \text{const.}, \quad . \quad . \quad (60)$$

or

$$\mathrm{F}(r) = \mathrm{A}r\,e^{-r^2/qv^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

The mean value of r^2, expressed by

$$\int_0^\infty r^3 \mathrm{F}(r)\,dr \div \int_0^\infty r\,\mathrm{F}(r)\,dr,$$

is qv^2 ; that is, the mean value of the maximum kinetic energy attained during the vibration is equal to the kinetic energy of a projectile. The mean of all the actual kinetic energies of the vibrators is the half of this ; but would rise to equality with the mean energy of the projectiles, if the velocities of the latter, instead of being uniform, as above supposed, were distributed according to the Maxwellian law.

If we are content to assume the *law* of distribution, $\rho\,e^{-h\rho^2}$, leaving only the constant h to be determined, the investigation may be much simplified. Thus from (57) the gain of energy from the collision is

$$\tfrac{1}{2}r^2 - \tfrac{1}{2}\rho^2 = 2q\rho\cos\phi\,(v - \rho\cos\phi) + 2q^2v^2.$$

The chance of the collision in question is proportional to the relative velocity $(v-\rho\cos\phi)$; and in the stationary state the whole gain of energy is zero. Hence

$$\iint \rho\, e^{-h\rho^2}\, d\rho\, d\phi \{2q\rho\cos\phi\,(v-\rho\cos\phi)^2+2q^2v^3\}=0.$$

In the integration with respect to ϕ the odd powers of $\cos\phi$ vanish. Hence

$$2qv\int_0^\infty \rho\, d\rho\, e^{-h\rho^2}(qv^2-\rho^2)=0\,;$$

so that

$$h=1/qv^2,$$

as in (61).

Terling Place, Witham,
August 19, 1891.

PM 32 (1891)

LIV. *On the Discharge of Electricity through Exhausted Tubes without Electrodes.* *By* J. J. Thomson, *M.A., F.R.S., Cavendish Professor of Experimental Physics, Cambridge.*

[Continued from p. 336.]

Phosphorescence produced by the Discharge.

THE discharge without electrodes produces a very vivid phosphorescence in the glass of the vessel in which the discharge takes place ; the phosphorescence is green when the bulb is made of German glass, blue when it is made of lead glass. Not only does the bulb itself phosphoresce, but a piece of ordinary glass tubing held outside the bulb and about a foot from it phosphoresces brightly ; while uranium glass will phosphoresce at a distance of several feet from the discharge. Similar effects, but to a smaller extent, are produced by the ordinary spark between the poles of an electrical machine.

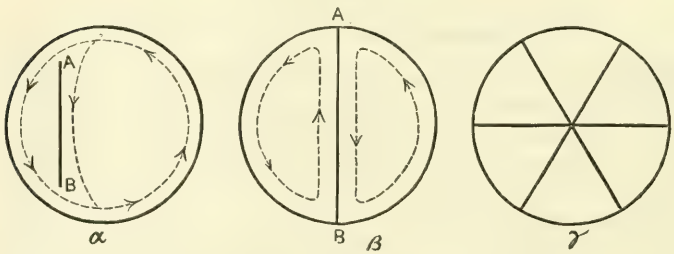
The vessel in which the discharge takes place may be regarded as the secondary of an induction-coil, and the discharge in it shows similar properties to those exhibited by currents in a metallic secondary. Thus no discharge is produced unless there is a free way all round the tube ; the discharge is stopped if the tube is fused up at any point. In order that the discharge may take place, it is necessary that the molecules of the gas shall be able to form a closed chain without the interposition of any non-conducting substance ; indeed the discharge seems to be hindered by the

presence in such a chain of any second body, even though it may be a good conductor of electricity. Thus, when a tube such as that in fig. 7 is used, which has a barometer-tube attached to it, so that by raising or lowering the vessel into which the tube dips a mercury pellet may be introduced into the discharge-circuit, the spark-length in the primary circuit may be so adjusted that a discharge passes when there is a clear way round the tube, but stops when a pellet of mercury is forced up so as to close the gangway. I noticed a similar effect in my experiments with a long vacuum-tube described in the Proceedings of the Royal Society for Jan. 1891.

Fig. 7.

I had another discharge-tube prepared, of which a section is shown in fig. 8, α, in which a diaphragm (AB) of thin copper plate was placed across the tube; the diaphragm happened to catch at the bottom of the tube, so that it divided the latter rather unequally, and left a narrow passage round its edge. As much of the discharge as there was room for went round the edge of the plate; the

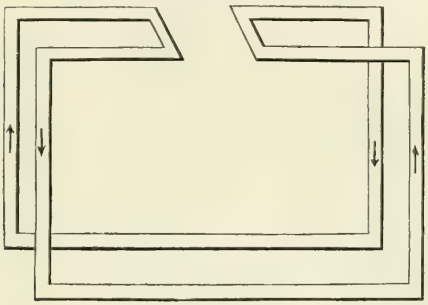
Fig. 8.



remainder was not able to get through the copper, but formed a closed circuit by itself in the larger segment of the tube. In another tube, which is represented in section in fig. 8, β, the copper diaphragm was attached to the walls of the tube by sealing-wax, so that there was no free way; in this case the discharge again refused to go through the copper, and split up into two separate discharges, as in the figure. When the tube was divided by copper diaphragms into six segments, as in fig. 8, γ, no discharge at all would pass through. When the primary was slipped up the tube above the diaphragm, a brilliant discharge was obtained. These four experiments all illustrate the difficulty which the electricity has in getting transferred from a gas to another conductor.

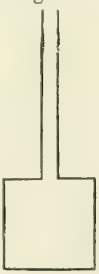
There is no discharge through the secondary, if it is of such a kind that, considering a closed curve drawn in it, the electromotive intensity as we travel along the curve tends to polarize the particles in one half of the chain in one direction, and in the other half in the opposite direction, the direction being reckoned relative to the direction we are travelling round the curve. Thus, for example, if we take a tube whose axis is bent back on itself, as in the figure, the electromotive intensity will tend to polarize the particles in one part of the chain in the direction of the arrow, and those in the other in the opposite direction ; it is impossible to get a discharge through a tube of this kind.

Fig. 9.



On the other hand, the molecules exhibit remarkable powers of making closed chains for themselves when not actually prevented by the action of the electromotive intensity. Thus the discharge will pass through a great length of tubing in the secondary, even if it is bent up as in fig. 10, where the vertical piece in the upper part of the secondary is at right angles to the direction of the electric force, and where the molecules will receive no help in forming closed chains from the action of the external electromotive forces. I have succeeded in sending discharges through tubes of this kind 12 to 14 feet in length.

Fig. 10.



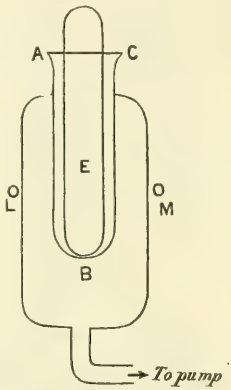
Screening Effects due to the Currents in the Tubes.

One very noticeable feature of these discharges is the well-defined character of the ring, if the pressure is not too low. If a large bulb is used for the secondary with the primary just outside it, when the sparks pass between the jars a

bright, well-defined ring passes through the bulb near to the surface of the glass, the gas inside this ring being, as far as can be judged, quite free from any discharge. If now a bulb whose diameter is less than that of the luminous ring is inserted in the primary in place of the larger bulb, a bright ring will start in this, though at this distance from the primary there was no discharge in the larger bulb. Thus when the large bulb was in the primary, the discharge through its outer portions screened the interior from electromotive forces to an extent sufficient to stop a discharge which would otherwise take place.

The screening action of these discharges is also shown by the following experiment. A, B, C, fig. 11, is the section of a glass vessel shaped like a Bunsen's calorimeter; in the inner portion A, B, C of this vessel an exhausted tube is placed, while a pipe from the outer vessel leads to a mercury pump and enables us to alter the pressure at will. The primary coil, L, M, is wound round the outer tube. When the air in the outer tube is at atmospheric pressure, the discharge caused by the action of the primary passes in the tube E inserted in A, B, C; but when the pressure in the outer tube is reduced until a discharge passes through it, the discharge in the inner one stops; the discharge in the outer tube has thus shielded the inner tube from the action of the primary. If the exhaustion of the outer tube is carried so far that the discharge through it ceases, that in the inner tube begins again. It requires very high exhaustion to do this, and as on account of the joints it is unsafe to make the vessel very hot during the pumping, I have found it impossible to keep a vacuum good enough to show this effect for more than from half to three quarters of an hour; in that time sufficient gas seems to have escaped from the sides of the vessel to make the pressure too high to show this effect, and it then takes from two to three hours' pumping to get the tube back again into its former state. An interesting feature of this experiment is that for a small range of pressure, just greater than that at which the discharge first appears in the outer tube, there is no discharge in either of the tubes; thus the action of the primary is screened off from the inner tube, though there is no luminosity visible in the outer one; this shows

Fig. 11.

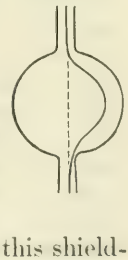


that a discharge equivalent in its effects to a current can exist in the gas without sufficient luminosity to be visible even in a darkened room. We shall have occasion to mention other cases in which the existence of a discharge non-luminous throughout the whole of its course is rendered evident in a similar way.

Another experiment by which the screening can be effectively shown is to place the primary coil inside a bell-jar which is connected with a mercury pump, the electrical connexions with the primary being led through mercury joints. An exhausted bulb is placed inside the primary, the bulb being considerably smaller than the primary, so that there is an air-space between the two. Before the bell-jar is exhausted the discharge passes through the bulb, but when the bell-jar is exhausted sufficiently to allow of the discharge passing through the gas outside the bulb the discharge in the bulb ceases, and the only discharge is that outside. I have never been able to exhaust the bulb sufficiently well to get the discharge outside the bell-jar to cease, and that in the bulb to appear again, as in the preceding experiment. In this experiment, as in the preceding one, there was a range of pressure when neither the bulb nor the bell-jar was luminous, showing again the existence of currents in the gas which are not accompanied by any appreciable luminosity.

A curious bending-in of the discharge which takes place in a square tube provided with a bulb can, I think, be explained by the principle of shielding. The discharge in the bulb does not, unless very long sparks are used, take as its course through the bulb the prolongation of the direction of the tube, but is bent-in towards the primary. In fig. 12 the dotted line represents the course the discharge would have taken if there had been no bulb, the continuous line the course actually taken. This bending-in can be explained by supposing the currents started near the primary to shield off from the outlying space the action of the primary, and thus make the electromotive intensity along the axis of the tube smaller than it would have been if no discharge had been possible between the axis and the primary circuit.

Fig. 12.



Before describing some further experiments on this shielding effect, it will be useful to consider the means by which it is brought about. Let us suppose we have a vertical plate made of conducting material, and to the right of the plate a

region A which it shields. This region has to be shielded from tubes of electrostatic induction coming from the left, which have to pass through the shield before reaching A, and from tubes coming from the right which have to pass through A before reaching the field. The action of the shield in the first case is very simple, for when a tube gets inside a conductor it at once attempts to contract to molecular dimensions, and after a time proportional to the specific resistance of the conductor it succeeds in doing so. Thus if the shield is made of a good conductor the tubes of electrostatic induction will be transformed into molecular tubes before they have time to get through; so that the shield will protect A from all tubes which have to go through it. The way the shield destroys or rather neutralizes the effect of the tubes coming from the right is somewhat different: when a positive tube reaches the shield a negative one emerges from it, travelling at right angles to itself in the opposite direction to the incident tube; thus when the first few tubes reach the shield from the right they will produce a supply of negative ones, and the presence of these negative tubes at A concurrently with the positive ones which continue to arrive there will weaken the field to a greater and greater extent as A approaches the shield. At the surface of the shield itself the neutralization will be complete. A dielectric whose specific inductive capacity is greater than usual will behave in a similar way to a metal plate, but to a smaller extent. It will emit tubes of the opposite sign, but not so numerous as those incident upon it. Thus a metal plate, or even one made of a dielectric of considerable specific inductive capacity, will reduce very considerably the tangential electromotive force on either side of it.

I have made several experiments in which this effect was very strikingly shown. In one of these, two square discharge-tubes of equal cross section placed near and parallel to each other were connected by a cross tube, so that the pressure was the same in both tubes; a fine wire passed round the inside of one of the tubes, its ends being connected together so that it formed a closed circuit, the other tube contained nothing but air at a low pressure. When this double tube was placed outside the primary the discharge went, at the passage of each spark, through the tube without a wire, while the tube containing the wire remained quite dark. A similar experiment was tried by taking a cylindrical tube and suspending in it a metal ring coaxial with the tube; in this case it was easy to adjust the spark-length so that no discharge

passed through the tube when the primary was placed round it at the level of the ring, while a discharge passed as soon as the primary was moved above or below the ring.

Another very convenient tube for showing this effect is the one with the hollow down the middle, fig. 11; when this is pumped so that discharges can pass through the outer tube the spark-length can be adjusted so that the discharge stops immediately when a metal tube, a test-tube containing a strong solution of an electrolyte, or a tube containing air at a pressure at which it is electrically very weak, is placed in the central opening. The discharge is renewed again as soon as the tubes are removed. On one occasion, when the large tube was in a peculiarly sensitive state, I was able to see distinctly the diminution produced by a dielectric in the electromotive intensity parallel to its surface. The discharge stopped as soon as a stick of sulphur or a glass rod sufficiently large almost to fill the opening was inserted, and was renewed again as soon as these were withdrawn. It requires, however, the large tube to be in an extremely sensitive state for the effect produced by a dielectric to be apparent, and I have only on one occasion succeeded in getting the tube into this condition. The effect on that occasion, however, was so definite and regular that I have no doubt as to the existence of the screening effect due to the dielectric.

When the tube is of average sensitiveness dielectrics do not produce any appreciable effect, nor can the influence of even comparatively so good a conductor as distilled water be detected, and it is not until after the addition of a considerable quantity, 10 to 20 per cent., of sulphuric acid or ammonium chloride, that the insertion or withdrawal of the tube stops or starts the discharge.

A tube containing air at a low pressure is very efficacious in stopping the discharge, and the result of the comparison of the relative effects of an exhausted tube and a tube of the same size and shape containing a solution of an electrolyte are very remarkable. I found that an exhausted tube which contained air at a very low pressure (less than $\frac{1}{10}$ of a millimetre) produced as much effect on the discharge in the outer tube as a tube containing at least 50,000 times as many molecules of ammonium chloride. This would be expressed in the language of electrolysis by saying that under the electromotive intensity to which it was exposed in this experiment the molecular conductivity of the gas is 50,000 times that of the electrolyte. The proportion between the number of air molecules and the number of molecules of an

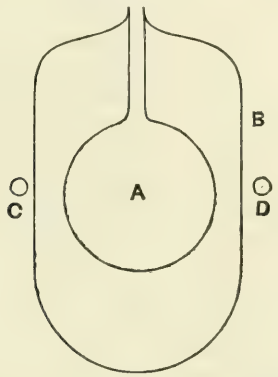
electrolyte, which produces an equal effect in stopping the discharge, depends upon the length of spark in the primary current, and so upon the electromotive force acting upon the air. The longer the spark the greater is the molecular conductivity of the air in comparison with that of the electrolyte. This indicates that the conduction through the air does not follow Ohm's law. This is what we should expect, as under large electromotive forces more molecules are split up and take part in the conduction of the electricity. This great conductivity of rarefied gases in those cases where the electricity has not to pass from metal &c. into the gas are in striking contrast with the infinitesimally small values for the same property which are deduced from experiments on tubes with electrodes.

I was first led to suspect this high conductivity for rarefied gases by observing the appearance presented by the ring-discharge in bulbs; the ring, unless the pressure is exceedingly low, ceases at a distance of little more than 1 centim. from the surface of the bulb, this thickness of conducting gas being sufficient to screen off the electromotive intensity from the interior. From experiments which I had made on the screening effect of electrolytes (Proc. Roy. Soc. xlv. p. 269), I knew that it would require a very strong solution of an electrolyte to produce screening comparable with this. To compare the screening effects more directly than by the method just described I tried the following experiment. The discharge-tube, fig. 11, was pumped until the discharge passed through it very freely; an exhausted tube was then pushed down the central opening, it remained quite free from any visible discharge; the primary was now wound round a cylinder of the same diameter as the discharge-tube of fig. 11, and this cylinder was filled with distilled water. When the tube, which had previously remained dark when placed in the exhausted discharge-tube, was immersed in the water, a brilliant discharge took place in it; and it was necessary to add about 25 per cent. of sulphuric acid to the water before the shielding effect of the mixture was sufficient to keep the tube dark. This experiment shows perhaps even more directly than the other the great conductivity of a rarefied gas under large electromotive forces when nothing but the gas is in the way of the passage of the current.

An experiment made in this connexion illustrates the remark made before as to the large effects produced by discharges through the gas which are not accompanied by luminosity. A bulb A was fused into a tube B which was

surrounded by the primary coil C, D. B was exhausted and then sealed off, while A was left connected to the pump. When A was at atmospheric pressure a bright discharge took place in B outside A; on pumping A a stage was reached in which no discharge could be seen in either A or B. On letting air into A the discharge appeared again in B; on pumping A still further a discharge appeared in A, but not in B. The appearance presented by the discharge round the

Fig. 13.



bulb A (filled in this case with air at high pressure) is very remarkable. At the highest pressure at which the discharge passed it took the form of a thin ring round the middle of A; as the pressure got lower and lower the discharge broadened out, and at very low pressures formed for the greater part of its course two separate rings which ran together in the space between one side of the sphere and the tube.

On the Effect produced by Conductors near the Discharge-tube.

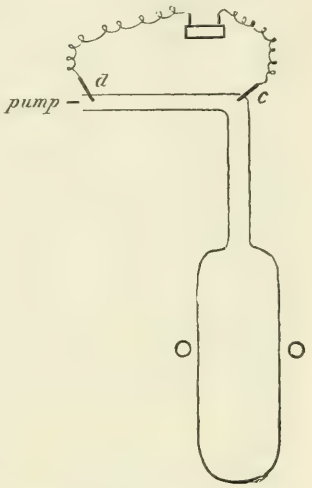
The intensity of the discharge is very much affected by the presence of conductors in the neighbourhood of the discharge-tube, especially conductors which have large capacity or which are connected to earth. Let us take, for example, a very simple case, that of a bulb surrounded by a primary which is connected to earth; in this case the approach of the hand, or any conductor connected to earth, will make the discharge brighter and at the same time less well-

defined at the edges; touching the tube, though this is already connected to earth, produces a very marked effect in increasing the facility of the discharge. We can, I think, understand the reason of this if we consider the behaviour of the tubes of electrostatic induction. When the spark passes, these tubes (see p. 327) rush out from the jars and make for the primary; in their journey to the primary they pass through the bulb and produce the discharge. Let us suppose now that there is a large conductor situated somewhere near the bulb; the tubes, as before, rush from the jar to the primary, but in doing so some of them strike against the conductor; the tubes which do so lose the portion inside the conductor, acquire two ends each on the surface of the conductor, and swing round until they are at right angles to its surface; they remain momentarily anchored, as it were, to the conductor, and if the conductor is in the neighbourhood of the bulb, they will in general help to increase the maximum density of the tubes passing through the bulb. Though these tubes may not approximate to closed curves, and so directly produce a ring-discharge, they may readily facilitate this discharge indirectly; for even those tubes which go radially through the bulb may produce a glow-discharge from the glass into the bulb, and may thus furnish a supply of dissociated molecules through which the ordinary ring-discharge can pass with much greater readiness. For nothing is more striking than the enormous difference produced in the electric strength of these rarefied gases by the passage of a spark. It is sometimes difficult to get the discharge to pass at first, but when once a spark has passed through the gas, a spark-length one quarter the length of that necessary to originate the discharge will be found sufficient to maintain it.

It is sometimes convenient, in cases where difficulty is found in starting the discharge, to avail ourselves of this property by connecting the mercury of the pump to which the tube is attached with one terminal of an induction-coil, the other terminal of which is put to earth. When the induction-coil is in action, a glow-discharge fills the pump and tube, and while this glow exists the electrodeless discharge can easily be started; once having been started, it will continue after the induction-coil is stopped. An experiment of this kind, which I had occasion to make, gave very clear evidence of the way in which dissociated molecules are projected in all directions from the negative electrode in an ordinary discharge-tube, but not from the positive. The discharge-tube was fused on to the pump, and at an elbow two terminals, *c* and *d*, fig. 14, were fused into the glass; these terminals were

connected with an induction-coil, and the pressure in the tube was such that the electrodeless discharge would not start of itself. When the coil was turned on so that *c* was the negative electrode, the electrodeless discharge in the tube at once took place, but no effect at all was produced when *c* was positive and *d* negative. We may thus regard the effect produced by the presence of a conductor as due to the conductor catching the tubes of electrostatic induction, and concentrating them on the discharge-tubes. These tubes in many cases acting indirectly by producing a glow-discharge through the tube, which, by diminishing the electric strength of the gas, makes discharges of any other kind very much easier. Though the presence of a conductor near the discharge-tube will, in general, concentrate the tubes of electrostatic induction on the discharge-tube more than would otherwise be the case, yet this does not always happen. When in some positions the conductor may hold back for a time from the discharge-tube tubes of electrostatic induction which would otherwise pass through it, and thus diminish the maximum density of the tubes of electrostatic induction in the discharge-tube, and hence tend to stop the discharge. I have frequently met with cases where the presence of a conductor diminishes the intensity of the discharge. One of the most striking of these is when the two jars are insulated, and a square discharge-tube used. The spark was adjusted so that the discharge just, but only just, went round the tube. A sphere connected to earth was then moved round the discharge-tube; in some positions it increased the brilliancy of the discharge, and the tube became quite bright, while in other positions it stopped the discharge altogether.

Fig. 14.

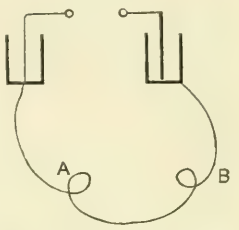


The observation of the behaviour of the discharges through these tubes is a very convenient method of studying the effect of conductors in deflecting the flow of the tubes of electrostatic induction which fall upon them; for the appearance of the discharge is affected not merely by the average, but also by the maximum value of the electromotive intensity which

produces it. Thus a high maximum value, lasting only for a short time, might produce a discharge, while a more equable distribution of electromotive intensity having the same average value might leave the tube quite dark.

I have employed these discharges to study the behaviour of bodies under the action of very rapid electrical oscillations in the following way. In the primary circuit connecting the outside coatings of the jar, two loops A and B (fig. 15) were made, in one of which, A, an exhausted bulb was placed, the spark-length and the pressure of the gas on it being adjusted until the discharge was sensitive, *i. e.* until a small alteration in the electromotive intensity acting on the bulb produced a considerable effect upon the appearance presented by the discharge. The substance whose behaviour under rapid electrical vibrations was to be examined was placed in the loop B. The results got at first were very perplexing, and at first sight contradictory, and it was some time before I could see their explanation. The following are some of these results. When a highly exhausted bulb was placed in B a brilliant discharge passed through it, while the discharge in A stopped. A bulb of the same size, filled with a dilute solution of electrolyte, produced no appreciable effect; when filled with a strong solution it dimmed the discharge in A, but not to the same extent as the exhausted bulb. A piece of brass rod or tube increased the brightness of the discharge in A ; on the other hand, a similar piece of iron rod or tube stopped the discharge in A at once. The most decided effect, however, was produced by a small crucible made of plumbago and clay : this when put in the loop B stopped the discharge in A completely. I found, however, that by considering the work spent on the substance placed in B, the preceding results could be explained. When a large amount of work is spent in B, the discharge in A will be dimmed, while no appreciable effect will be produced on A when the work spent in B is small. Now let us consider the work done in a secondary circuit whose resistance is R, whose coefficient of self-induction is L, and which has a coefficient of mutual induction M with the primary circuit. If the frequency of the current circulating in the primary is p, we can easily prove that the rate of absorption of work by the secondary is proportional to

Fig. 15.



$$\frac{\mathrm{R\,M^2}p^2}{\mathrm{L^2}p^2+\mathrm{R^2}}.$$

Thus the work given to the secondary vanishes when R=0 and when R=infinity, and has a maximum value when R=Lp. Thus the condition that the secondary should absorb a considerable amount of work is that the resistance should not differ much from a value depending on the shape of the circuit and the frequency of the current in the primary. No appreciable amount of work is consumed when the resistance is very much greater or very much less than this value. I tested this result by placing inside B a coil of copper wire. When the ends were free, so that no current could pass through it, it produced no effect upon the bulb in A ; when the ends were joined so that there was only a very small resistance in the circuit, the effect was, if anything, to increase the brightness of the discharge in A. When, however, the ends were connected through a carbon resistance which could be adjusted at will, the discharge in A became very distinctly duller when there was a very considerable resistance in the circuit. This experiment confirms the conclusion that to absorb energy the resistance must lie within certain limits, and be neither too large nor too small.

We can now see the cause of the differences observed when the substances mentioned above were put into B. The brass rod and tube did not dim the discharge in A, because their resistance was too low ; the weak solution of electrolyte, because the resistance was too great; while the resistances of the crucible and the strong solution of electrolyte which obliterated the discharge from A were near the value for which the absorption of energy by the system was a maximum.

The case of iron is very interesting because it shows that even under these very rapidly alternating forces, iron still retains its magnetic properties. A striking illustration of the difference between iron and other metals is shown when we take an iron rod and place it in B, the discharge in A immediately stops; if we now slip a brass tube over the iron rod the discharge in A is at once restored. If, on the other hand, we use a brass rod and an iron tube, when the rod is put in B without the tube the discharge in A is bright; if we slip the iron tube over the rod, the discharge stops.

To compare the amount of heat produced in the brass and iron secondaries, let us take the case of an infinite cylinder exposed to an external magnetic force parallel to the axis equal to $H_0\epsilon^{ipt}$.

If H is the magnetic force inside the cylinder at a distance r from the axis, H satisfies the differential equation

$$\frac{d^2H}{dr^2} + \frac{1}{r}\frac{dH}{dr} = \frac{4\pi\mu}{\sigma}\frac{dH}{dt},$$

or, since H varies as $\epsilon^{\iota pt}$,

$$\frac{d^2H}{dr^2} + \frac{1}{r}\frac{dH}{dr} - n^2H = 0;$$

where $n^2 = 4\pi\mu\iota p/\sigma$; μ being the magnetic permeability of the cylinder, and σ its specific resistance. The solution of this equation is

$$H = A\, J_0(\iota nr)\epsilon^{\iota pt},$$

where J_0 denotes Bessel's function of zero order. Since the magnetic force outside the cylinder is not affected by the currents we must have, if a is the radius of the cylinder,

$$A\, J_0(\iota na) = H_0.$$

Thus

$$H = H_0 \frac{J_0(\iota nr)}{J_0(\iota na)}\epsilon^{\iota pt}.$$

The currents induced in the cylinder are tangential, and if q is the intensity of the current at a distance r from the axis of the cylinder,

$$4\pi q = -\frac{dH}{dr}$$

$$= -\iota n H_0 \frac{J_0'(\iota nr)}{J_0(\iota na)}\epsilon^{\iota pt}.$$

We shall consider two special cases: first, where the resistance is so great that na is a small quantity; this includes the case of the plumbago crucible and the tube filled with the electrolyte.

In this case we have approximately

$$J_0(\iota na) = 1,$$

$$J_0(\iota nr) = -\tfrac{1}{2}\iota nr.$$

Thus

$$4\pi q = -\tfrac{1}{2}n^2 r\epsilon^{\iota pt}$$

$$= -\frac{2\pi\mu\iota p}{\sigma} H_0 r\, \epsilon^{\iota pt}.$$

Taking the real part of this expression we find

$$q = \frac{\mu p}{2\sigma} H_0 r \sin pt.$$

The rate of heat-production per unit length of the cylinder is

$$\int_0^a \sigma q^2 2\pi r\, dr,$$

the average value of which is

$$\frac{H_0^2}{16\sigma} \cdot \pi\dot{\mu}^2 p^2 a^4.$$

As this is proportional to the conductivity, the best conductors will absorb the most energy.

The other case which we shall consider is that in which na is very large. This applies to the metal tubes and rods.

In this case,

$$J_0(\iota nr) = \frac{\epsilon^{nr}}{\sqrt{2\pi nr}} \text{ approximately.}$$

Thus

$$4\pi q = -n\epsilon^{-n(a-r)} \left\{ \frac{a}{r} \right\}^{\frac{1}{2}} \epsilon^{\iota pt},$$

$$n\epsilon^{-n(a-r)} = \alpha + \iota\beta.$$

Then taking the real part of the expression for q,

$$4\pi q = -\left\{ \frac{a}{r} \right\}^{\frac{1}{2}} (\alpha \cos pt - \beta \sin pt).$$

The rate of heat-production is again

$$\int_0^a \sigma q^2 2\pi r \, dr ;$$

the mean value of which is

$$\frac{a}{8\pi} \frac{1}{2} \int_0^a \sigma(\alpha^2 + \beta^2) dr$$

$$= \frac{a\sigma}{16\pi} \int_0^a \frac{4\pi\mu p}{\sigma} \epsilon^{-(a-r)\sqrt{\frac{8\pi\mu p}{\sigma}}} dr$$

$$= \frac{a}{8\sqrt{2\pi}} \sqrt{p\mu\sigma},$$

and is thus proportional to the square root of $\mu\sigma$. Hence for iron and copper cylinders of the same dimensions it would be about 70 times as large in the iron as in the copper, assuming that the iron retains its magnetic properties under these very rapidly alternating forces. The result explains the effect of the iron in stopping the discharge. As I am not aware that any magnetic properties of iron under such rapidly alternating forces have been observed, I was anxious to make quite sure that the difference between iron and brass was not due solely

to the differences between their specific resistances. The first experiment I tried with this object was to cover the iron rod with thin sheet platinum, such as is used for Grove cells. As the resistance of platinum is not very different from that of iron, if the effect depended merely upon the resistance, slipping a thin tube of platinum over the iron ought to make very little difference. I found, however, that when the platinum was placed over the iron, all the peculiar effects produced by the latter were absent, thus showing that the effect is not due to the resistance of the iron. It then occurred to me that I might test the same thing in another way by magnetizing the iron to saturation, for in this state μ is nearly unity; thus if the result depended mainly on the magnetic properties of the iron it ought to diminish when the latter is strongly magnetized. I accordingly tried an experiment in which the iron in the coil B was placed between the poles of a powerful electromagnet. When the magnet was "off" the iron almost stopped the discharge in A; when it was "on" the discharge became brighter, not indeed so bright as if the iron were away altogether, but still unmistakably brighter than when it was unmagnetized. This experiment, I think, proves that iron retains its magnetic properties when exposed to these rapidly alternating forces.

Another result worthy of remark is that though a brass rod or tube inserted in B does not stop the discharge in A, yet if a piece of glass tubing of the same dimensions is coated with Dutch metal, or if it has a thin film of silver deposited upon it, it will stop the discharge very decidedly. We are thus led to the somewhat unexpected result that a thin layer of metal when exposed to these very rapid electrical vibrations may absorb more heat than a thick one. I find, on calculating the heating-effect in slabs of various thicknesses, that there is a thickness for which the heat absorbed is a maximum. Instead of taking the case of a cylinder, for which the analysis is somewhat long, I will take the case (which is physically almost equivalent to it) of a plain electrical wave incident normally upon a plane sheet of metal.

Let the electromotive intensity E in the incident wave be represented by the real part of the equation

$$\mathrm{E} = \epsilon^{\iota(pt+ax)},$$

the axis of x being at right angles to the plate, and the origin on the upper surface of the plate. The electromotive intensity E_1 in the wave reflected from the plate may be represented by the equation

$$\mathrm{E}_1 = b\epsilon^{\iota(pt-ax)}.$$

In the metal the electromotive intensity satisfies the equation

$$\frac{d^2\mathrm{E}}{dx^2} = \frac{4\pi\mu}{\sigma}\frac{d\mathrm{E}}{dt},$$

so that the electromotive intensity E_2 inside the plate may be represented by the equation

$$\mathrm{E}_2 = \epsilon^{\iota pt}\{\mathrm{A}\epsilon^{-m(1+\iota)x} + \mathrm{B}\epsilon^{m(1+\iota)x}\},$$

where

$$m = \{2\pi\mu p/\sigma\}^{\frac{1}{2}}.$$

On the far side of the plate the electromotive intensity E_3 is given by

$$\mathrm{E}_3 = c\epsilon^{\iota(pt+ax)}.$$

To determine the coefficients b, c, A, B, we have the conditions that at the surface of the plate, *i. e.* when $x=0$, and when $x=-h$, h being the thickness of the plate :—

(1) The electromotive intensity is continuous;

(2) The magnetic force parallel to the plate is continuous. This implies that $\frac{1}{\mu}\frac{d\mathrm{E}}{dx}$ is continuous.

From (1) we get

$$1+b = \mathrm{A}+\mathrm{B},$$

$$c\epsilon^{-ah} = \mathrm{A}\epsilon^{m(1+\iota)h} + \mathrm{B}\epsilon^{-m(1+\iota)h};$$

while from (2),

$$a(1-b) = (1+\iota)\frac{m}{\mu}(\mathrm{A}-\mathrm{B}),$$

$$ac\epsilon^{-ah} = -(1+\iota)\frac{m}{\mu}(\mathrm{A}\epsilon^{m(1+\iota)h} - \mathrm{B}\epsilon^{-m(1+\iota)h}).$$

We can simplify these equations if we remember that for electrical vibrations as rapid as those we are now considering $m/a\mu$ is exceedingly large. Introducing this condition we find

$$\mathrm{A} = \frac{2a\mu}{m(1+\iota)}\frac{\epsilon^{-m(1+\iota)h}}{\epsilon^{m(1+\iota)h} - \epsilon^{-m(1+\iota)h}},$$

$$\mathrm{B} = \frac{2a\mu}{m(1+\iota)}\frac{\epsilon^{m(1+\iota)h}}{\epsilon^{m(1+\iota)h} - \epsilon^{-m(1+\iota)h}}.$$

Thus in the metal plate the electromotive intensity is given by the equation

$$\mathrm{E}_2 = \frac{2a\mu}{m(1+\iota)}\frac{1}{\epsilon^{m(1+\iota)h} - \epsilon^{-m(1+\iota)h}}\{\epsilon^{-m(1+\iota)(x+h)} + \epsilon^{m(1+\iota)(x+h)}\}\epsilon^{\iota pt}.$$

Let

$$\frac{2a\mu}{m(1+\iota)}\,\frac{1}{\epsilon^{m(1+\iota)h}-\epsilon^{-m(1+\iota)h}}=\alpha+\iota\beta.$$

Then, taking only the real part of the expression for E_2, we have

$$E_2=\epsilon^{m(h+x)}\{\alpha\cos(pt+m(h+x))-\beta\sin(pt+m(h+x))\},$$
$$+\epsilon^{-m(h+x)}\{\alpha\cos(pt-m(h+x))-\beta\sin(pt+m(h+x))\}.$$

The rate of production of heat per unit volume of the plate is E_2^2/σ; the mean value of this at a point whose coordinate is x is

$$\frac{1}{2\sigma}(\alpha^2+\beta^2)\{\epsilon^{2m(h+x)}+\epsilon^{-2m(h+x)}+2\cos m(h+x)\}.$$

To get the rate of heat-production per unit area of the plate, we must integrate this with respect to x between the limits $x=0$, $x=-h$. Performing this integration we find that the rate of production of heat per unit area of the plate is

$$\frac{1}{4m\sigma}(\alpha^2+\beta^2)\{\epsilon^{2mh}-\epsilon^{-2mh}+2\sin 2mh\}.$$

Substituting for $\alpha^2+\beta^2$ its value this becomes

$$\frac{2a^2\mu^2}{4\sigma m^3}\,\frac{(\epsilon^{2mh}-\epsilon^{-2mh}+2\sin 2mh)}{(\epsilon^{2mh}+\epsilon^{-2mh}-2\cos 2mh)}.$$

To compare this with the expression we found for the solid cylinder, we notice that if $H_0\epsilon^{\iota pt}$ is the magnetic force in the incident wave at the surface of the plate,

$$H_0^2p^2=a^2.$$

So that the rate of heat-production per unit area may be written

$$\frac{1}{2}\frac{H_0^2\mu^2p^2}{\sigma m^3}\,\frac{(\epsilon^{2mh}-\epsilon^{-2mh}+2\sin 2mh)}{(\epsilon^{2mh}+\epsilon^{-2mh}-2\cos 2mh)},$$

$$=\frac{H_0^2}{8\sqrt{2}}\left\{\frac{\mu\sigma p}{\pi}\right\}^{\frac{1}{2}}\left\{\frac{(\epsilon^{2mh}-\epsilon^{-2mh}+2\sin 2mh)}{(\epsilon^{2mh}+\epsilon^{-2mh}-2\cos 2mh)}\right\}.$$

The part of this expression involving h is equal to unity when mh is very great, that is for a thick plate; it is, however, greater than unity for some values, the smaller values of h for which it is a maximum satisfying the equation

$$\sin 2mh(\epsilon^{2mh}-\epsilon^{-2mh})=0.$$

When h vanishes the rate of heat-production, as given by the preceding expression, is infinite. We have, however, in this expression used approximate values for A and B. If we use their accurate values we find that the rate of heat-production vanishes when $h=0$, but rises very quickly to a large value as h increases.

The slight increase in the brightness of the discharge in A when a brass rod is placed in B is due, I think, to the diminution in the self-induction in the primary circuit produced by this rod, whose conductivity is so good that it absorbs practically no heat.

We will now return to the case of bad conductors, where na is small; here the absorption of energy is proportional to the conductivity, and we might use this method to compare the conductivity of electrolytes for very rapidly alternating currents. I tried a few experiments of this kind, and found, as I did in the experiments described in the 'Proceedings' of the Royal Society, xlv. p. 269, that the ratio of the conductivities of two electrolytes was the same for rapidly alternating as for steady currents. I was anxious, however, to see whether these rapidly alternating currents could pass with the same facility as steady currents from an electrolyte to a metal. To try this, two equal beakers were filled with the same electrolyte made of such strength that when inserted in B they put out the discharge in A. I then placed in one beaker six ebonite diaphragms arranged so as to stop the eddy currents, and a similar metallic diaphragm in the other. The ebonite diaphragm made the beaker in which it was placed cease to have any effect upon the discharge in A. I could not detect, however, that the effect of the beaker in which the metal diaphragm was placed on the discharge in A was at all diminished by the introduction of the diaphragm. I conclude, therefore, that very rapidly alternating currents can pass with facility from electrolytes to metals, and *vice versâ*. In this respect electrolytes differ from gases, the currents in which, as we have seen, are stopped by a metallic diaphragm in the same way as they would be by an ebonite one.

It may be useful to observe, in passing, that a somewhat minute division of the electrolyte by the non-conducting diaphragm is necessary to stop the effect of the eddy currents; a division of the electrolytes into two or three portions seemed to produce very little effect.

Another point which is brought out by these experiments is the great conductivity of rarefied gases when no electrodes are used as compared with that of electrolytes. An

exhausted bulb will produce as much effect on the discharge in A as the same bulb filled with a solution of an electrolyte containing about a hundred thousand times as many molecules of electrolyte. The molecular conductivity of rarefied gases when the electromotive intensity is very great and when no electrodes are used must be thus enormously greater than that of electrolytes.

Bulbs filled with rarefied gas used in the way I have described serve as galvanometers, by which we can estimate roughly the relative intensity of the currents flowing through the primary coils which encircle them. Used for this purpose, I have found them very useful in some experiments on which I am at present engaged on the distribution of very rapidly alternating currents among a network of conductors.

I have much pleasure, in conclusion, in thanking my assistant, Mr. E. Everett, who has done the whole of the very large amount of glass-blowing required for these experiments, and has rendered very efficient help in other parts of the work. My thanks are also due to Mr. A. T. Bartlett, B.A., for the assistance he has given on several occasions.

Cambridge, July 1891.

LV. *Some Remarks suggested by a popular Article on the Ignis Fatuus.* By Charles Tomlinson, *F.R.S., F.C.S., &c.**

A NUMBER of distinguished scientific men form a committee of the British Association for encouraging the teaching of science in elementary schools. In their Report for 1889 they say :—"This year has been one of continued depression in regard to the teaching of science in elementary schools, and of disappointment in regard to legislative action." In their Report for 1890, however, their object is said to be more hopeful of attainment, seeing that the New Code is favourable thereto, although it is a matter of regret that no special arrangement has been made for the instruction of pupil-teachers in some branch of science.

In our middle-class schools, science and modern languages apparently require to be more systematically studied than they are at present, if we as a nation would maintain our commercial and manufacturing position with respect to other countries. There is hope that the various Polytechnic Institutions that are scattered about will supply the want. I have

* Communicated by the Author.

been honorary examiner in Physics to the Birkbeck Institution during many years, and can bear ample testimony to the excellence of its scientific teaching.

There is, however, a good deal of indifference in private life as to whether science is taught or not, or how it is taught. In some cases this indifference is based upon ignorance of the importance of such knowledge ; in other cases there is a decided prejudice against it, because it is supposed to conflict with certain theological dogmas.

Even when such prejudices are absent, there is a want of discrimination in the selection of text-books for the young, and it is often a mere chance if a book written by a competent hand is selected.

I was led into these reflections by a passage that was recently submitted to me from a book on Popular Science which has passed through many editions. It professes to give an account of the *Ignis Fatuus.*

"This luminous appearance (which haunts meadows, bogs, and marshes) arises from gas of putrefying animal and vegetable substances, especially from decaying fish. These luminous phantoms are so seldom seen because phosphoric hydrogen is so very volatile that it generally escapes into the air in a thinly diffused state. They fly from us when we run to meet it, because we produce a current of air in front of ourselves (when we run towards the *ignis fatuus*) which drives the light gas forwards. It runs after us when we flee from it, because we produce a current of air in the way we run, which attracts the light gas in the same course, drawing it after us as we run away from it. The Welsh 'corpse candles' are the same thing as the *ignis fatuus.* Swarms of luminous insects passing over a meadow sometimes produce an appearance similar to the *ignis fatuus.*"

It is impossible to suppose that this account was written by a scientific chemist ; it was probably the work of one of those gentlemen in the Reading-Room of the British Museum who disturbed Mr. Carlyle in his studies :—"The use they make of the Library," he said, "is to assist them in drawing up articles for Compilation, Dictionaries, and Encyclopædias, and the stuff called 'Useful Knowledge.' They are a very thick-skinned race."*

The gentlemen thus referred to are often greatly indebted to the Cyclopædias in getting up books of Popular Science. But though the Cyclopædias themselves have been greatly

* Evidence before the Commissioners appointed to inquire into the Constitution and Management of the British Museum, 1849.

improved of late years, seeing that they owe many of their leading articles to competent writers, yet it must be admitted that the very considerable number of short articles are entrusted to inferior hands. I was anxious to see how such compilers might be led, or misled, by consulting the article *Ignis Fatuus* in three well-known Cyclopædias. The first reference is to the "English Cyclopædia" (Arts and Sciences Division), 1860, where there is a short article under *Ignis Fatuus*, a meteor resembling a flame which is vaguely said to do a number of things and may be seen over marshes or burial-grounds, and a case is related in which a weak blue flame came up from the sea, and burnt some ricks of hay. It is also stated that "such meteors are most usually witnessed during a fall of rain or snow." After referring to some other cases the writer remarks, "Little confidence can be placed in the descriptions given of them, as few persons have been able to examine them with due attention; and commonly they have been observed under the influence of an ill-regulated imagination rather than a philosphical spirit." That such meteors are due to phosphuretted or carburetted hydrogen gas is termed "a plausible hypothesis," but "there is a great dearth of satisfactory observations on moving lights seen in nature, and the entire subject is at present in obscurity."

The second example is from the *Encyclopædia Britannica*, ninth edition, 1885, where the subject, oddly enough, is treated in a few lines under *Phosphorescence*, which is said to be "a name given to various phenomena due to different causes, but all consisting in the emission of a pale, more or less ill-defined light, not obviously due to combustion." It is stated that *Ignis Fatuus*, as seen in marshy districts, has given rise to much difference of opinion. Kirby and Spence suggested that it might be due to luminous insects, "but it is more reasonable to believe that the phenomenon is caused by the slow [?] combustion of marsh-gas."

In Chambers's Cyclopædia, "A Dictionary of Universal Knowledge," New Edition, vol. vi. 1890, we have much excellent writing in the longer articles, and only a feeble grasp of subject in some of the shorter ones. There is the same uncertainty in the treatment of *Ignis Fatuus**, and the same confusion as in the earlier writers, arising from the application of the same term to meteors of very different origin. The article begins by stating that *Ignis Fatuus* "is a luminous appearance of uncertain nature which is occa-

* This article seems to have been entirely derived from the article *Irrlichter* in the *Konversations-Lexicon.*

sionally seen in marshy places and churchyards. The phenomenon has been frequently described, but it has been observed so rarely in favourable circumstances by scientific men, that there is no satisfactory explanation." The theory that the meteor is due to ignited marsh-gas is dismissed as untenable, because the gas does not ignite spontaneously. The more plausible suggestion that it is due to phosphuretted hydrogen, which ignites on contact with oxygen, is also rejected, on the ground that a German observer, named List, "passed his hand through the luminous appearance, and felt no warmth;" while another German, named Knorr, "held the metal-tip of a walking-stick in the flame of a fixed *ignis fatuus*... for a quarter of an hour, but the metal was not warmed."

References to these observations are not given; but the luminous appearances were probably not gaseous, but electrical, as was also the meteor, which was seen to "bound over the country like a ball of fire for half an hour at a time."

The scientific reader cannot fail to see that these notices in works of so much pretension, and of such recent dates, are quite unworthy of their fame. It is also curious to notice how the descriptions of earlier writers, with their ignorance of gases and imperfect knowledge of electricity, have stimulated the timid doubts of the modern compiler. One example from an old writer, and in many respects an admirable one, may here be quoted, namely, Dr. Van Musschenbroek, Professor of Mathematics and Philosophy in the University of Leyden*. In his Latin treatise on Natural Philosophy, vol. ii. page 291, is the following paragraph:—

"§ 1329. *Wandering fires*, or *Ignes Fatui*, are of a round figure, in bigness like the flame of a candle, but sometimes broader, and like bundles of twigs set on fire. They sometimes give a brighter light than that of a wax candle, at other times more obscure, and of a purple colour. When viewed near at hand, they shine less than at a distance. They wander about in the air, not far from the surface of the earth, and are more frequent in places that are unctuous, muddy, marshy, and abounding with reeds. They haunt burying places, places of execution, dunghills. They commonly appear in summer, and at the beginning of autumn. But in the country about *Bononia*, they are seen throughout the whole year in a

* This work was written in Latin, and was first published in 1726; it was reprinted in 1734, and again in 1762, each time with considerable augmentations. It was translated by John Colson, M.A., and F.R.S., Lucasian Professor of Mathematicks in the University of Cambridge, and was printed for J. Nourse at the *Lamb*, without *Temple Bar*, 1744.

dark night. For there in a cold winter, and when the ground is covered with snow, they are in greater plenty than in the hottest summer. Those also are observed in winter, which *Gassendus* says are seen at *Rogon*, a town of *Provence*. They appear more frequently in hot than in cold countries. In *Italy* near *Bononia* are the greatest, and in greatest plenty. Sometimes they vanish on a sudden, and presently shine out in another place. They are generally at the height of about six feet from the ground. Now they dilate themselves, and now contract. Now they go on like waves, and rain as it were sparks of fire, but they burn nothing. They follow those that run away, and fly from those that follow them. Some that have been catched were observed to consist of a shining, viscous, and gelatinous matter, like the spawn of frogs, not hot or burning, but only shining; so that the matter seems to be phosphorous, prepared and raised from putrefied plants or carcases by the heat of the sun; which is condensed by the cold of the evening, and then shines. Yet I do not think that the matter of all is the same, for without doubt those of Bononia differ from those of Holland. It is a mere fiction that these fires are evil spirits or wandering ghosts, misleading travellers out of mere spite, to plunge them into ditches and bogs as some trifling Philosophers have told us."

In the above passage there is much admirable description of the *Ignis Fatuus*, but the writer cannot reconcile the phenomena as due to one source, for he does not think that "the matter of all is the same." It is clear that some of the phenomena refer to *gaseous* meteors, others to *electrical*, and others again to *phosphorescent**, but further advances in natural knowledge were required before these distinctions could be made clear.

The first step towards a true explanation of the *Ignis Fatuus* was taken by Priestley, who, in 1767, began his "Experiments and Observations on different kinds of Air," and thus

* In the Philosophical Magazine for August and December 1888 I have cited a number of examples of low lying electrical meteors. These may be multiplied to almost any extent, but they must not be confounded with the *ignis fatuus*. Whether phosphorescent lights are ever seen hovering over graves, forming what are called "corpse candles," has not been decided by scientific evidence unless the testimony of Reichenbach's sensitive patients be taken as such. Some years ago the inhabitants of a small town in Scotland were alarmed by a luminous appearance in the neighbouring wood. It was seen during several evenings after sunset. Most of the inhabitants were too timid to investigate the cause, but one bold spirit ventured and found the light to proceed from a large putrescent fish which some one had thrown up into a tree.

laid the foundation of Pneumatic Chemistry. Among his experiments are a considerable number on the inflammable air produced during the decomposition of various kinds of vegetable, and in vol. i., page 209, he says :—"The air from marshes also, which, with Sig. Volta, I doubt not comes from putrefying vegetable substances, I have also found to be equally permanent;" that is, not absorbed by water, as in the case of fixed air.

The name of Volta makes me pause for a moment to express my astonishment that Professor Kämtz, of the University of Halle, in his celebrated *Lehrbuch der Meteorologie*, published in 1832, in the section on *Irrlichter oder Irrwische* (*Ignes fatui*, *Ambulones*, *Feux follets*), expresses his opinion, and notes it as a remarkable fact, that no physicist has specially examined the nature of these lights (vol. ii. p. 490), and yet he gives a multitude of authorities most of whose observations are of very little value, except in the case of Volta, who, as he says, supposed that marsh-gas or carburetted hydrogen is the cause of these lights, and that the gas is kindled by means of an electric spark*.

Now it is surprising that Kämtz, with his extensive knowledge of scientific literature, relating in any way to Meteorology, should have ignored a work published in 1787, on Meteors, by the Abbé Bertholon, Professor of Experimental Physics at Languedoc, and member of various scientific societies. Taking advantage apparently of Priestley's discoveries, for, as he appropriately remarks, it was impossible to explain the *Ignis Fatuus* before gases were discovered, he describes a capital experiment which we must hear him relate in his own language :—

"Il est bien prouvé, par l'expérience et l'observation, que, dans les marais et les terrains marécageux, il y a de l'air inflammable ; il suffit, pour en obtenir, de remuer avec une canne la vase de ces endroits, aussitôt on verra s'en échapper, à travers de l'eau qui en couvre plus ou moins la surface, une quantité assez considérable. Si dans cet instant on approche la lumière d'une bougie on verra aussitôt l'air inflammable s'allumer, et la flamme s'étendre au loin." †

The gas thus formed has often been collected in bottles full of water inverted over the spot ; it was found by Sir Humphry Davy and others to contain carbonic acid and a small quantity of nitrogen, the proportion of either or both of which would of course influence the character of the flame.

* His reference is to Volta, Opere iii. p. 46.
† Tome Second, p. 10.

Many years ago, Major Blesson, of Berlin, made a number of experiments in a valley in the Forest of Gubitz, in the Newmarck, where the meteor was often seen. The valley cuts deeply into compact loam, and is marshy at its lower part. The water of the marsh contains iron, and is covered with a shining crust. During the day, bubbles of gas were seen rising from it, and at night bluish-purple flames were observed playing over the surface. On visiting the spot by night, the flames retired as the Major advanced, the motion of the air driving the burning gas before him. On standing still, the flames returned, and he tried to light a piece of paper at them ; but the current of air produced by his breath kept the flames at too great a distance. On turning away his head, and screening his breath, he set fire to a strip of paper. He also succeeded in putting out the flame by driving it before him to a part of the ground where no gas was produced ; then, applying a flame to the place whence the gas bubbles issued, a kind of explosion was heard over eight or nine square feet of the marsh ; a red light was seen, which faded to a blue flame about three feet high, and this continued to burn with an unsteady motion. As the morning dawned the flames became pale, and seemed to approach nearer and nearer to the earth, until at last they faded from sight. The same observer also made experiments in other places. At Malapane, in Upper Silesia, he passed several nights in a forest where the meteor was to be seen. He succeeded in extinguishing and inflaming the gas, but was not able to set fire to thin strips of paper or shavings of wood by its means. In the Komski Forest, in Poland, the flame appeared of a darker hue than usual, and on attempting to ignite paper and wood they became covered with a viscous kind of moisture, thus reminding one of Musschenbroek's observation when an *ignis fatuus* was "catched." On another occasion he succeeded in lighting up the *ignis fatuus* by standing at a distance and throwing fire-works into the marshy ground. He visited by night the summit of the Porta Westphalia, near Minden ; the meteor was not visible, but on firing off a rocket a number of small red flames were observed below, which soon went out, but appeared again on firing another rocket*.

In conclusion, it seems scarcely necessary to remark that writers in Cyclopædias and Popular Guides to Science have abundant sources of reliable information if they will only

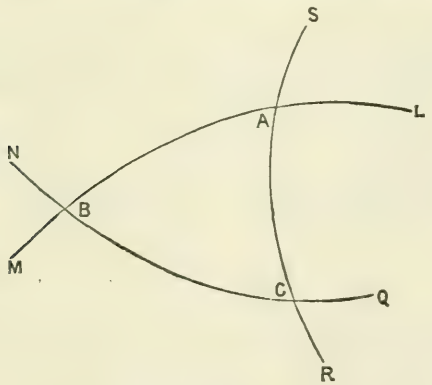
* I have mislaid the reference to Major Blesson's experiments, but the account given above is from a book on Natural Phenomena, written by me for the Christian Knowledge Society, and published in a second edition in 1858.

take the trouble to look in the right places: for there cannot be any ground for the doubts cast upon the subject in the articles above quoted; seeing that the *ignis fatuus* is produced by the ignition either by lightning or by accidental flame of light carburetted hydrogen or marsh-gas which is generated by the decay of vegetable matter in boggy places; and the reason why the phenomenon is now so seldom seen is that these places have been drained and brought under cultivation.

Highgate, N., 4th August, 1891.

LVI. *On a Theorem in Plane Kinetic Trigonometry suggested by* Gauss's *Theorem of Curvatura Integra.* *By* Sir WILLIAM THOMSON*.

1. ALBERT GIRARD'S beautiful theorem of the "Spherical Excess," in spherical trigonometry published about 1637, and used practically 150 years later by General Roy in the trigonometrical survey of the British Isles, was splendidly extended by Gauss in his theorem† of the "Curvatura Integra." There must be a corresponding theorem in the



"kinetic trigonometry" suggested in the marginals of Thomson and Tait's 'Natural Philosophy,' §§ 301 (*a*) (*b*) (*c*) (*d*), for the motion of the generalized conservative kinetic system of any number of variables. For the very simple case

* Communicated by the Author.

† "Disquisitiones Generales circa Superficies Curvas: auctore Carolo Frederico Gauss; Societati Regiæ [Gottingensi] Oblatæ D.VIII. Octobr. MDCCCXXVII." Collected Works, Vol. IV. Göttingen 1873. Thomson and Tait's Natural Philosophy §§ 131 .... 138.

of a material point moving in a plane it is easily worked out, as I have found in endeavouring to write a continuation of my article (Philosophical Magazine, October) on the Periodic Motion of a Finite System, which I hope may be ready to appear in the December number. Here is the theorem meantime.

2. Let L A B M, N B C Q, R C A S be three paths of a particle moving freely in a plane, under influence of a force $\left(\frac{-dV}{dx}, \frac{-dV}{dy}\right)$ and projected from any three places in any direction in the plane, with such velocities that the sum of the kinetic and potential energies has the same value (E) in each case. The sum of the three angles A, B, C exceeds two right angles by an amount which, reckoned in radian, is equal to the surface-integral of $\nabla^2 \log \sqrt{(E-V)}$, throughout the enclosed area A B C; ∇^2 denoting the Laplacian operation $\frac{d^2}{dx^2} + \frac{d^2}{dy^2}$.

3. To prove this; remark that

$$\iint dx\, dy \nabla^2 \psi = \int ds \frac{d\psi}{dn},$$

where ψ denotes any function of (x, y); $\iint dx\, dy$ surface-integration throughout any area; $\int ds$ line-integration all round its boundary; and $\frac{d\psi}{dn}$ rate of variation of ψ in the direction perpendicular to the boundary at any point. Hence the surface-integral mentioned in § 2 is equal to

$$\int ds \frac{-dV}{2(E-V)dn} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

But $\frac{-dV}{dn}$ is the normal-component force (N, we shall call it); and $2(E-V)$ is the square of the velocity (v^2, we shall call it). Hence (1) becomes

$$\int ds \frac{N}{v^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

But N/v^2 is the curvature ($\frac{1}{\rho}$, we shall call it), at any point in any one of the three arcs A B, B C, C A. Hence, dividing $\int ds$ into the three parts belonging respectively to these three

arcs, which we shall denote by $\int_A^B ds$, $\int_B^C ds$, $\int_C^A ds$, we find for (2),

$$\int_A^B \frac{ds}{\rho} + \int_B^C \frac{ds}{\rho} + \int_C^A \frac{ds}{\rho} . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

But $\int_A^B \frac{ds}{\rho}$ is the change of direction in the arc A B, and similarly for the two others : hence the theorem.

LVII. *On the Nature of Solution. By* J. Alfred Wanklyn, W. Johnstone, *and* W. J. Cooper*.

THE venerable Dalton made the great discovery, about the year 1840, that contraction occurs when salts dissolve in water. In some instances the contraction is so great that the volume of the solution of the salt is not greater than that of the water itself—the contraction being as large as the volume of the anhydrous salt existing in the solution. Dalton experimented upon the same salt in its hydrated and in its anhydrous condition, and he also extended his investigation to a great variety of salts, and his results he sums up as follows† :—"I have tried the carbonates, the sulphates, the nitrates, the muriates or chlorides, the phosphates, the arseniates, the oxalates, the citrates, the tartrates, the acetates, &c., &c., and have been uniformly successful : only *the water adds to the bulk*, and *the solid matter adds to the weight*."

Such was the condition in which Dalton left this subject about the year 1840.

Taking up the investigation where Dalton left off, we find that in the majority of cases there is indeed considerable contraction when salts dissolve in water, but that the degree of contraction varies very widely with different salts. In some instances in which mineral matter dissolves in water, the contraction is so great that the volume of the solution is actually less than the volume of the water which forms it. This is strikingly exemplified by lime-water, which occupies less space than the water which it contains. On the other hand, there are cases where the volume of the solution of a mineral salt is almost as great as the sum of the volume of the salt plus the volume of the water in the solution. (The solution of nitrate of silver is a case in point.) There are even instances where expansion takes place. This is exemplified

* Communicated by the Authors.

† Henry's 'Life of Dalton' (Cavendish Society), p. 193.

by some ammoniacal salts, where the volume of the solution has been found to exceed the sum of the volumes of water and dry salt.

Finally, there is the very important and, we think, very common case where solution takes place without any change of volume whatever. Such a case is afforded by solutions of cane-sugar*, which dissolves in water in almost all proportions, and the solutions of which occupy exactly the same volume as the separate water and sugar which enter into them.

A characteristic example of solution is afforded by sugar and water; and we hold that solution is mutual permeation without change of volume, as exemplified by sugar and water.

The changes of volume so frequently observed, in the instance of mineral salts, are due to chemical action, which is often a concomitant of solution.

In order to trace the connexion between the specific gravity of solutions and the composition of solutions, the following method may be followed with advantage.

We regard solutions as being generated by the entrance of successive units of weight into a large unit of volume. The unit of weight is one gramme. The unit of volume is 100 cubic centim., or one litre. The unit of volume is taken to be constantly filled with the solvent except in so far as it is occupied by the thing dissolved.

i = the increment-coefficient; that is to say, the increment of weight occasioned by the entrance of one gramme of the substance into 100 cubic centim., or one litre of solution. It is found experimentally by weighing the 100 cubic centim. or the litre of the solution, and subtracting the weight of 100 cubic centim. or a litre of the pure solvent. If the solution contains more or less than one gramme of the substance in the 100 cubic centim. or litre of solution, the number of grammes must be ascertained and used as a divisor.

When one gramme of a substance is inserted into 100 cubic centim. occupied by a solvent, one of three things must happen:—

(1) There may be absolutely no change in volume—neither contraction nor expansion. When one gramme of mercury is dropped into 100 cubic. centim. of water there is neither contraction nor expansion, and the gramme of mercury simply displaces its own volume of water, which overflows out of the 100 cubic centim. measure. Sp. gr. being the specific gravity of mercury, the quantity of water which

* *Vide* Chemical News (1891) vol. lxiv. p. 27, Wanklyn and Cooper.

overflows will be $\frac{1}{\text{sp. gr.}}$: and the increment of weight in that case would be

$$1-\frac{1}{\text{sp. gr.}}.$$

Such a value we represent by i_1.

$$i_1=1-\frac{1}{\text{sp. gr.}}.$$

This is the case of sugar, and no doubt of many organic substances which simply dissolve in water without chemical action of any kind.

(2) There may be contraction. This is exemplified by common salt and water. When one gramme of common salt is inserted into 100 cub. centim. of water, the displaced water is partly condensed and retained in the 100 cub. centim.

$$i-i_1=\text{the condensate ;}$$

that is to say, the weight of the water which, instead of overflowing, is retained in the vessel when one gramme of salt dissolves so as to give 100 cub. centim. of the solution.

(3) There may be expansion. In such a case when one gramme enters the 100 cub. centim. or the litre a larger quantity than $\frac{1}{\text{sp. gr.}}$ will overflow and

$$i-i_1 \text{ becomes a minus quantity.}$$

This is exemplified by chloride of ammonium, which undergoes decomposition when it is dissolved in water, and the volume of the solution of that salt actually exceeds the sum of the volumes of the water and the salt in their separate condition.

In a series of papers which have recently appeared in the 'Chemical News,' we have treated solution from this point of view, and shown that the condensate $(i-i_1)$, in the case of very many salts, bears an atomic relation to the gramme of salt which occasions it.

Sugar and Water.

The ordinary tables of the specific gravities of solutions of different strengths are constructed so as to mask the regularity of the relation between specific gravity and strength. The common sugar table, for instance, gives the specific gravities corresponding to the strength represented in percentage by weight. That mode of statement hides the regularity ; but when the table is transformed so as to set out

strength in terms of the number of grammes of sugar in 100 cub. centim. of solution, then there are indications of regularity. By a very obvious method of calculation this transformation may be effected. The ordinary tables when so treated exhibit some departure from regularity.

We have undertaken a revision of the table and our result is that these departures from regularity are experimental errors.

Our results are as follows :—

	Number of grms. of Cane-Sugar in litre of solution.	Specific Gravity.	i.
° Fahr.			
65·5	1·341	1000·52	·3878
54	1·341	1000·52	·3878
53·7	1·341	1000·52	·3878
53·7	9·878	1003·84	·3887
56·0	104·580	1040·60	·3882
59·0	749·50	1282·00	·3762

In these experiments we have compared the weight of the sugar-solutions with the weight of an equal volume of distilled water at the same temperature as the sugar-solution, and in each instance have used a half-litre specific-gravity bottle *, except in the last experiment.

The last measurement was made with a 100 cub. centim. bottle, and has not the same claim to be considered highly accurate as the other five measurements ; and we attribute the slight difference in that case to experimental error, and to another cause which may be considered hereafter.

The value of i for sugar we find therefore to be ·388, and it is constant over a very wide range, viz., from 1 grm. of sugar per litre of solution up to 750 grm. of sugar per litre of solution.

The specific gravity of solid sugar required in order to make $i_1 = ·388$ is 1·634. The specific gravity of sugar is given in the text-books as 1·606†, which would make $i_1 = ·3773$.

Sugar, therefore, presents an example of equality between i and i_1 ; that is to say, its solutions in water occupy exactly the same volume as the separate water and sugar which form them.

At the beginning of this paper we called attention to Dalton's discovery of the contraction which takes place when

* *Vide* Wanklyn's 'Water Analysis' (Kegan Paul, Trench, and Trübner), eighth edition, p. 78.

† *Vide* Watts's 'Dictionary of Chemistry,' vol. v. p. 470.

salts dissolve in water. Dalton also experimented upon sugar, but failed to notice that in that case there is no contraction; and it has been reserved for ourselves, after the lapse of half a century, to record that there are cases, such as that of sugar, where there is rigid maintenance of volume.

Laboratory, New Malden, Surrey.

LVIII. *Notices respecting New Books.*

Theorie der Quaternionen. Von Dr. P. Molenbroek. Leiden, 1891.

WE are told in the Preface that this theoretical volume, of 284 pages, is to be followed immediately by another containing systematized applications. It is to be hoped, rather than expected, that this second volume will not exhibit the prolixity and the uncalled-for minuteness of detail which purposely characterize the first. We say *purposely* because, though Dr. Molenbroek states that Hamilton's great Treatise (which is accessible to continental readers in a German translation) is so extensive in its theoretical part as to frighten readers away from the applications, he complains that the work of Prof. Tait (also accessible in translations) gives an inadequate (*dürftig*) account of the theory. Hence his own work is designed to occupy a position midway, as it were, between these two treatises. And it does so more by laboriously spinning out the parts treated by Tait, than by introducing other material from Hamilton's stores.

When we examine the work itself, we find that Dr. Molenbroek's notions as to the really important parts of the theory differ very widely from those of Hamilton and his pupil. So far as we can discover, there is not in his work even an allusion to ∇! How the promised applications, if they are to deal at all with potentials, fluid motion, &c., are to be made in the second volume, must therefore for the present remain a mystery. On the other hand, the subject of powers and roots of quaternions, not at present of much use in applications, is developed at disproportionate length.

But the novel feature of the work, and one to which special attention is directed in the Preface, is of a really startling character; inasmuch as it is entirely at variance with the elementary definitions given by Hamilton, and reproduced by Dr. Molenbroek himself! Comment on such a proceeding is altogether unnecessary. We need do no more than state that he regards an imaginary *scalar* multiplier as an undetermined *quadrantal quaternion*, which has the singularly felicitous but hitherto unsuspected power of adjusting its axis so as to be perpendicular to any vector to which it may be applied! His volume of examples and applications will certainly be eagerly expected, if it is to contain other gems like that enunciated (p. 104) in the following words:—

"Man kann somit sagen, ein doppelbrechender Krystall könne wie ein konisch spaltender Quaternion wirken."

We have hitherto admired Hamilton's wonderful dealings with

the geometrical interpretation of the *vector* $\sqrt{-1}$. Its *scalar* form would appear to have even more singular and important properties and applications. But, alas for Dr. Molenbroek, Hamilton long ago said:—and his words are final:—"the *old* and ORDINARY IMAGINARY SYMBOL of common algebra . . . . is to be treated . . . . *not* as a *real vector* . . . . *but* as an *imaginary scalar*." Sic transit gloria M——!

LIX. *Intelligence and Miscellaneous Articles.*

CHEMICAL ACTION AT A DISTANCE.

BY S. U. PICKERING, F.R.S.

IN the Philosophical Magazine for August (p. 145) there appears a paper by Prof. Ostwald bearing this somewhat theatrical title: in it the author describes some experiments for which, in his opinion, "a satisfying explanation can be first gained on the ground of the *Theory of free ions*," and which, having been "worked out at [his] writing-table *before* [he] *had seen anything of the phenomena in question* . . . . speak," he considers, "more forcibly than any polemics for the value of this theory." The object of the present note is to try and elicit some explanation as to what the difficulty is in explaining, or even predicting, the facts on the old theory of electrochemical action, and why they are to be regarded as affording any proof of the truth of the dissociation theory.

The chief experiment is as follows:—A zinc-platinum couple is placed in a solution of potassium sulphate, and on adding sulphuric acid to the liquid near the platinum the acid is decomposed with liberation of hydrogen while the zinc goes into solution, whereas, when the acid is added to the liquid near the zinc, no action occurs. The explanation of such a result appears to be perfectly simple without the aid of the dissociation hypothesis. We have only to remember that a zinc-platinum couple will not decompose potassium sulphate, but will decompose sulphuric acid, and that these effects will, in all probability, remain unaffected by the slight modification of the ordinary contacts obtaining in Prof. Ostwald's experiment: also that in all salt-solutions there is a continual interchange going on between the ions in contiguous molecules, which interchange involves no expenditure of work. That being so, the action will be represented by the following scheme:—

$$\overset{+}{Zn} \quad SO_4 \vdots K_2 \quad SO_4 \vdots K_2 \quad SO_4 \vdots H_2 \quad \overset{-}{Pt}.$$

No work, or only an infinitesimal amount, is done in transferring the K_2 from one SO_4 to the next: no potassium sulphate is really decomposed, for there are as many molecules of it present after as there were before the reaction; and the only body which is decomposed is the acid, a decomposition which we know a zinc-platinum couple will effect. The following scheme shows that if the acid is placed in contact with the zinc no decomposition could occur unless the couple were capable of decomposing the potassium sulphate, which it is not.

$$\overset{+}{Zn} \quad SO_4 \vdots H_2 \quad SO_4 \vdots K_2 \quad SO_4 \vdots K_2 \quad \overset{-}{Pt}.$$

Such an explanation appears to me to be much more simple than one which involves the idea that neutral zinc, when placed in a neutral solution, shoots off positive ions, leaving the remaining portion of the metal negative; the electric charges which convert the atoms into ions consisting of a something, and the charging being accomplished in a manner, of which, as Prof. Ostwald admits (p. 148), no explanation can be given.

Other experiments are quoted which seem no less inconclusive than the above in favour of the dissociation theory. The slow dissolution of copper in weak oxygenated sulphuric acid would seem to be explained at least as well on the view that the copper is first oxidized, and that the oxide of copper then dissolves (copper oxide, but not metallic copper, being capable of doing so with evolution of heat), as on the view that the hydrogen ions of the acid are oxidized, and thus give place for the copper ions shot off from the metal. The dissolution of gold in chlorine-water obviously requires no recourse to the free ion theory for an explanation; nor does the following experiment, which practically closes the list of Prof. Ostwald's "proofs." A beaker containing ferrous-chloride solution is connected, by means of a siphon containing sodium-chloride solution, with another beaker containing chlorine solution: on inserting connected platinum plates into the beakers a current passes, and the ferrous chloride becomes chlorinated to ferric chloride. Here the platinum in the one beaker is slightly acted on by the chlorine, and therefore becomes electropositive towards the platinum in the beaker with the ferrous chloride; the latter platinum consequently becomes electronegative, the iron atoms in its proximity become more than usually electropositive, being thereby rendered capable of attaching to themselves more chlorine, according to the following scheme:—

$$\begin{array}{ccccccccccccc} & & Fe\overset{Cl}{\underset{Cl}{}} & Cl \vdots FeCl & Cl \vdots FeCl & Cl \vdots Na & Cl \vdots Na & Cl \vdots Cl & & \\ \overset{-}{Pt} & & & & & & & & & \overset{+}{Pt}. \\ & & Fe\overset{Cl}{\underset{Cl}{}} & Cl \vdots FeCl & Cl \vdots FeCl & Cl \vdots Na & Cl \vdots Na & Cl \vdots Cl & & \end{array}$$

It is perhaps more probable that the chlorine atoms which the sodium atoms on the extreme right combine with are derived, not directly from the chlorine molecules as represented in this scheme, but from molecules of hydrochloric acid or platinum chloride present in the liquid. The chlorination of the ferrous chloride naturally occurs with those molecules which are nearest to the negative platinum, as Prof. Ostwald observes is the case. It is difficult to see why such an experiment should be regarded as a proof of the dissociation theory.

All these experiments seem to be on a par with one described some time ago by Prof. Ostwald, consisting in the production of a

small amount of electrolysis by a current of electrostatic origin: experiments which are perfectly consistent with the old electrochemical theory, dressed up in the garb of the dissociation theory, and then presented to us as proof positive of this theory.

MEASUREMENT OF THE CHEMICAL INTENSITY OF THE SOLAR RADIATION. BY A. BARTOLI.

The author raises the objection to previous investigations on this subject, that exothermal chemical processes have in many cases been used in which the heat developed must have a disturbing influence. The apparatus of the author consists of two metal vessels fitting one in the other, the inner one of which has a capacity of 7 litres; this is filled with water which has been boiled and then saturated with carbonic acid, and closed air-tight with a glass plate. Carefully selected subaqueous plants were placed in the water. This physiological actinometer was exposed to the sun's rays, and the quantity of oxygen found was determined. At the same time the action of heat and the brightness of the solar radiation was measured. With different heights of the sun the ratio of the oxygen disengaged to the strength of the radiation was almost constant.—*Boll. dell Acad. di Catania*, Jan. 1891; *Beiblätter der Physik*, vol. xv. p. 418.

ON WHEATSTONE'S DETERMINATION OF THE VELOCITY OF ELECTRICITY. BY PROF. J. STEFAN.

Kirchhoff, in his paper on the Motion of Electricity in Wires, first showed in 1857 that, under certain conditions, electricity moves in a thin wire according to the laws of wave-motion, and with a velocity which may be put equal to that of light. The agreement between the velocities of electricity and light is only attained when the first travels in a straight wire stretched in the air. Kirchhoff has restricted his investigation to this case. If the bases of his calculation are applied to other cases, for instance to a wire which is wound in a zigzag, or is coiled in a spiral, it is found that electricity travels in such a wire with far greater velocity. In Wheatstone's well-known experiment a wire was used which was coiled in twenty straight windings, and the velocity of electricity was found to be half as great again as that of light. I think that in the preceding I have given the right explanation of this result. I have, however, attempted to give this explanation an experimental support, and have employed the method given by Hertz of producing stationary waves in wires. I used a circuit like that in Wheatstone's experiment, but on a smaller scale, connected it with a couple of long straight wires, and compared the length of the wave in the circuit with the length of the same wave in the straight wires. The wave in the circuit is considerably longer, and in conformity with this the velocity of electricity in the circuit is greater than in the straight wires, and, according to my experiments, in a ratio which exceeds that found by Wheatstone.—*Wiener Berichte*, April 23, 1891.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

DECEMBER 1891.

LX. *The Influence of Surface-Loading on the Flexure of Beams.* *By* Prof. C. A. CARUS WILSON*.

[Plate II.]

THE practical treatment of the problem of beam-flexure at the present time is based on the hypothesis enunciated by Bernoulli and Euler†, that the bending-moment is proportional to the curvature.

This assumes that the cross sections remain plane after flexure and neglects the surface-loading effect.

Saint-Venant has shown‡ that the first assumption is untenable; but that, neglecting the surface-loading, Bernoulli's results are strictly true for one particular case of loading, that, namely, of a beam doubly supported and carrying a single isolated load, where, although the cross sections are distorted, the central displacement is zero.

I propose in this paper to describe some experiments made with a view to determining the actual state of strain in a beam doubly supported and centrally loaded, the surface-loading effect being taken into account.

The method of investigation adopted is based upon the following assumptions:—

(1) The true state of strain at the centre of the beam may be found by superposing on the state of strain due to bending only, that due to surface-loading without bending.

* Communicated by the Physical Society: read June 26, 1891.

† Todhunter and Pearson's 'History of Elasticity,' vol. i.

‡ Pearson's 'Elastical Researches of Saint-Venant.'

(2) The state of strain due to surface-loading only may be found, with close approximation to truth, by resting the beam on a flat plane instead of on two supports.

(3) The strains due to bending only may be obtained from the Bernoulli-Saint-Venant results; viz.:—

(α) The stretch for any cross section varies as the distance from the neutral axis.

(β) The central axis is unstretched.

(γ) For the same point in different cross sections the stretch varies as the bending-moment.

Saint-Venant has dealt with the shearing-strains at some little distance from the load in the case of a beam doubly supported and centrally loaded*; and Professor Pearson has shown† that, in the case of beams continuously loaded, the results of the Bernoulli-Eulerian theory can only be considered as giving approximate formulæ when the span of the beam is not less than ten times its depth‡.

The mathematical determination of the state of strain produced by the loading of a beam as it rests on a flat plane is one of considerable analytical difficulty.

MM. Lamé and Clapeyron have attempted the solution of a more general problem in their "Mémoire sur l'équilibre intérieur des corps solides homogènes."§ The object of this paper is stated to be "to investigate the way in which the interior of a body is affected by the transmission through it of the action of forces." Here they treat the problem of a solid extending to infinity on one side of a plane, on which is a given distribution of tractive load, and also of a solid contained between two parallel infinite planes. They obtain as a result a set of definite integrals giving the displacements, introducing a function involving the distribution of tractive load, from which the stresses may be deduced, but concerning which they add: "Les formules précédentes, pour être obtenues en séries numériques et immédiatement applicables, exigent la connaissance des valeurs d'un genre particulier d'intégrales définies, dont il ne nous paraît que les géomètres se soient encore occupés."

The most successful attempt at a solution of this problem is

* Pearson's 'Elastical Researches of Saint-Venant,' §§ 69–99.

† Pearson, "On the Flexure of Heavy Beams subject to continuous systems of Load," Quarterly Journal of Mathematics, No. 93 (1889).

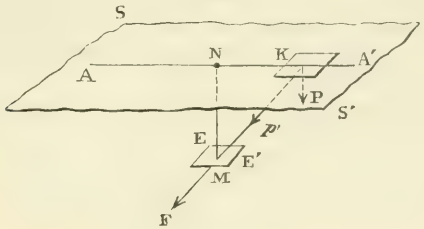
‡ Rankine assumed that the surface-loading effect might be neglected. See his 'Applied Mechanics,' § 311.

See also *Résumé des Leçons* &c. by Navier (Paris: Dunod, 1864), vol. i. p. 41:—"Observation sur le mode d'application et de distribution des forces qui font fléchir," where the same assumption is made.

§ Crelle's *Journal*, vol. vii. p. 145 *et seq.*

to be found in a more recent work by Professor Boussinesq, published in 1885*. The following is a brief account of the results obtained.

Fig. 1.



S S′ being the surface of the solid (infinite below in length, width, and depth), M a point within, situate at a distance M N = x below the surface, K any element of the surface, situate at the distance K M = r from the point M, and subject to a given exterior pressure K P = p, having the component K P′ = p' along K M, the pressure which a plane element E E′ taken through M parallel to the surface S S′ will support, per unit of area, in consequence of the pressure p, will be found directed along the direction of K M produced, and will be equal to

$$\mathrm{MF} = \frac{3p'x}{2\pi r^3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If, as a particular case, the pressure K P = p be normal, then $p' = p \cos \mathrm{NMK} = p\,\frac{x}{r}$, and

$$\mathrm{MF} = \frac{3px^2}{2\pi r^4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If, further, it is required to find the vertical component of MF, we have (MF) $\frac{x}{r}$, or

$$\frac{3px^3}{2\pi r^5}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The treatment of this particular problem is not pursued any further in this work; but Professor Boussinesq has kindly furnished me with a solution more nearly applicable to the

* *Application des Potentiels à l'étude de l'Equilibre et du Mouvement des Solides élastiques* (Gauthier-Villars, Paris, 1885).

See also *Théorie de l'Elasticité des Corps solides*, Clebsch; translated and annotated by MM. de Saint-Venant and Flamant. (Paris: Dunod, 1883, p. 374, note to art. 46.)

case in point, and one which will be found to agree closely with the experimental results I had previously arrived at, and which are given later on.

Suppose there to be a uniform pressure p exerted over every element du of bearing-surface between two extremities A, A′ (see figure), having abscissæ $u=-\mathrm{NA}=-a$, $u=\mathrm{NA}'=+a$, and let $p=\mathrm{P}du$, calling P the constant exterior pressure per unit of length $\mathrm{AA}'=2a$.

The total pressure over unit of surface of an element E E′ will be, from equation (3),

$$\Sigma\frac{3px^3}{2\pi r^5}=\int\frac{3\mathrm{P}x^3du}{2\pi r^5}=\frac{3\mathrm{P}x^3}{2\pi}\int_{-a}^{+a}\frac{du}{r^5}$$

$$=\frac{3\mathrm{P}x^3}{\pi}\int_0^a\frac{du}{(x^2+u^2)^{\frac{5}{2}}}\,[\mathrm{NK}=u].$$

Putting $\frac{u}{x}=\alpha$, $du=x\,d\alpha$, we get as the normal pressure per unit of area on E E′,

$$\frac{3\mathrm{P}}{\pi x}\int_0^{\frac{a}{x}}(1+\alpha^2)^{-\frac{5}{2}}d\alpha\;;$$

or, very nearly, if x is much smaller than a,

$$\frac{3\mathrm{P}}{\pi x}\int_0^{\infty}(1+\alpha^2)^{-\frac{5}{2}}\,d\alpha.$$

The value of the integral is $\frac{2\alpha^3+3\alpha}{3(1+\alpha^2)^{\frac{3}{2}}}$ or $\frac{2+\frac{3}{\alpha^2}}{3\left(1+\frac{1}{\alpha^2}\right)^{\frac{3}{2}}}$, which, between the limits $\alpha=0$ and $\alpha=\infty$, becomes $\frac{2}{3}$. Thus the pressure per unit of area on an element E E′ becomes $\frac{2\mathrm{P}}{\pi x}$, or

$$0{\cdot}64\,\frac{\mathrm{P}}{x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This expression has the form of that given below, though, inasmuch as the problem is not altogether the same as that treated experimentally*, a difference in the coefficients is only what might have been expected.

* The mathematical solution assumes the length of bearing A A′ on an infinite surface.

The value of the integral between the limits $\alpha=0$ and $\alpha=\infty$ is, as has been stated, $\frac{2}{3}$, or 0·667. For $\alpha=5$, *i. e.* for $u=5x$ as the upper limit, the integral = 0·666, and for $u=2x$ the integral = 0·656; so that this solution is approximately correct for elements lying at a distance of $\frac{1}{4}$ the width of the beam from the point of contact.

Hence for a beam where the length A A′ is 5·5 millim., this solution would be applicable up to points lying at a distance of about 1·4 millim. from the top surface.

I have investigated the law up to within 0·5 millim. of the top surface, and find it to be

$$y=0\cdot726\ \frac{P}{x}.$$

The investigation of the state of strain in glass beams by means of polarized light was first suggested by Sir David Brewster*, and his experiments are usually quoted as proving the truth of the Bernoulli-Eulerian theory of flexure. It is, however, easy to show experimentally that these experiments must have been made under conditions where the surface-loading effect was inappreciable; though very accurate reasoning on this point is impossible, as the drawings accompanying Sir David Brewster's paper are not to scale, and the span of the beams and the precise method of application of the loads are not indicated.

M. Neumann developed a theory of the action of strained glass in the polariscope†, and found that the velocity of light in a medium is increased by compressing it. He bases his calculations on the measurement of the deflexions of glass beams supposed to obey the Bernoulli-Eulerian theory; the beams are doubly supported and centrally loaded, having the proportions $66\times8\cdot5\times2$, the latter being the depth. It is not in all cases stated what spans were employed, so it is impossible to say how far the results were influenced by surface-loading.

Professor Clerk-Maxwell‡ has examined the state of strain in pieces of unannealed glass of various shapes, the lines of equal intensity of strain being deduced from the isochromatic lines.

The lines of Principal Stress are found from those of Equal Inclination in the manner described later on in this paper.

* Phil. Trans. 1818, p. 156.

† *Abhandlungen der k. Akademie der Wissenschaften zu Berlin*, 1841, vol. ii. pp. 50–61.

‡ Trans. Roy. Soc. Edinburgh, vol. xx. (1853) p. 117.

It has already been pointed out* that "Neither Neumann nor Maxwell seems to have remarked that the difference of the velocities of the ordinary and extraordinary rays depends solely on the maximum slide of planes perpendicular to the wave-front."

An important work on this subject is found in a paper by Dr. John Kerr†. He establishes the fact that "If a plate of glass, compressed or extended in one direction parallel to its faces, be traversed normally by two pencils of light, which are polarized in planes respectively parallel and perpendicular to the direction of strain, then both pencils are retarded by the strain in the case of compression, and both are accelerated by the strain in the case of tension." Also that "strain-generated retardations, absolute as well as relative, are sensibly proportional to the strain," thus confirming Wertheim's results.

Dr. Kerr employs in his experiments a bent glass beam, doubly supported and centrally loaded, having the ratio of span to depth‡ of 8·4 to 1, and assumed to obey the Bernoulli-Eulerian theory.

I would draw attention to the disagreement between the results arrived at by M. Neumann and Dr. Kerr, the former stating that the velocity of light in a medium is increased by compressing it, while the latter states that the velocity is diminished.

Dr. Kerr examined a beam having a span equal to 8·4 depths, and at a point where the surface-loading effect would be least; whereas M. Neumann examined a beam—span to depth ratio not stated—immediately under the load.

I can only attempt to account for the discrepancy by pointing out that if the span is diminished to less than four depths, the elements of glass that M. Neumann assumed to be in a state of squeeze are actually, as will be shown later, in a state of stretch.

The instrument with which the following experiments were made consists of a steel straining-frame in which the beam to be examined is placed; the beam rests—for flexure—on two steel rollers, and is loaded by a micrometer-screw which bears on a third central roller. The base of the frame is divided, from the centre, in divisions of 2 millim. so that the supports can be set for any required span. A micrometer-screw is placed in the base of the frame opposite the load, so that deflexions can be measured to one ten thousandth of an

* Hist. of Elasticity, vol. i. p. 643.
† Phil. Mag. October 1888.
‡ According to the figure.

inch. Two screws in the two sides of the frame enable lateral pressure to be applied. The whole frame can be moved in any direction in its own plane, so that all parts of the beam may be examined. The optical arrangements consist of two nicols, of which the upper is provided with a graduated disk on which the angle of rotation can be observed; a microscope with micrometer-eyepiece can be fitted when it is desired to measure the fringes; circularly polarized light can be used when required.

The beams used were marked on one side with 2 millim. squares; they were covered with paraffin and marked in a dividing-engine and then etched; the lines thus formed enabled the position of dark bands to be determined with accuracy.

Proposition I.

If a beam of glass be laid on a flat surface and loaded across its upper surface, the shear at any point on the normal at the point of contact of the load is inversely proportional to the distance from the point of contact.

Experiment 1. A beam of annealed glass 61 millim. × 6·5 millim. × 20 millim. deep was placed in the steel straining-frame with its narrow side resting on a piece of thin paper.

A steel roller 2 millim. in diameter, 10 millim. long, was placed across the middle of the top surface and loaded by the screw.

The nicols were crossed and at 45° to the axis of the beam.

A quarter-wave mica plate was placed between the beam and the analyser, with the plane containing the optic axes at right angles to the length of the beam.

At that point a on the normal where the difference of phase between the ordinary and extraordinary pencils traversing the beam is equal and opposite to the difference of phase produced by the mica plate—the effect will be as if there were no strained glass between the two nicols, and there will therefore be a black spot as the nicols are crossed.

The position of this spot on the normal is plotted on a sheet of squared paper, and an ordinate parallel to the axis chosen to represent the shear.

A second quarter-wave plate is now superposed on the first, and the black spot consequently moves up the normal to where the shear is twice what it was at a; this point, b, is noted, the second mica plate removed, and the load reduced until the black spot with one mica plate is brought to b. In this way a series of points a, b, c, d on the normal are found at any one of which the shear is twice what it is at the point below.

Now it is proved later on that the strain at any point

varies as the load on the beam; hence by taking the ordinate at b twice that at a, at c four times, and at d eight times, and so on, the get points on the curve of loading along the normal for the load that gives a difference of phase at a equal to that of one-quarter wave-plate.

The results are plotted on Plate II. fig. 1: the observed points are indicated by circles, through one of which an hyperbola has been drawn taking the normal and the upper surface of the beam as asymptotes.

It will be seen that the six upper circles lie very nearly on the hyperbola.

It is clear that the upper surface of the beam is an asymptote only when the surface of contact between the beam and the roller is a line—making the stress there infinite; but in practice this cannot be so, the smallest pressure giving a bearing surface—as the roller indents the beam—making the stress there finite, *i. e.* the asymptote will be at some finite distance θ, say, above the point of contact, and θ will vary with the load. I have calculated below that with a load of 115·3 lb. on this same beam, the value of θ is 0·044 millim.

The apparently irregular position of the two lower points observed indicates the amount of error made in the assumption (2) above that the surface-loading effect may be found by substituting a flat plane instead of two supports.

This assumption would be correct only if the beam were of infinite depth and the surface-loading effect of the support infinitely small; here, however, the steel frame itself produces a surface effect, and this, added to that due to the load, makes the points observed lie off the hyperbola, which would be the true curve (as drawn) if the beam were of infinite depth.

The effect of the steel frame must be very small compared with that due to the load for points in the upper half of the beam. In drawing the hyperbola I have considered it as negligible at the centre of the beam; in other words, I consider that the correction of the position of the six upper points, required to allow for the surface effect of the frame, would not make them deviate seriously from the hyperbola.

It must be noted, however, that when the beam is resting on two supports the surface effect of the frame disappears, since the beam only touches the supports and surface effect can only be caused by actual contact; hence I conclude that the surface effect due to loading only is strictly represented by the hyperbola and is as if the beam were of infinite depth*.

* According to this reasoning there appears to be a shear of finite amount at the bottom of the beam—when doubly supported—due to loading only, but this does not seem to me to be inconsistent with the surface conditions.

In order to establish the hyperbolic law with greater certainty, experiments were made enabling as many as seven points on the curve to be obtained within 3·5 millim. of the point of contact, the highest point being about ·5 millim. from the top of the beam.

Within this range the effect due to the steel frame may with accuracy be neglected.

Experiment 2. A beam of annealed glass, 61 millim. × 6·5 millim. × 20 millim. deep, was placed in the steel straining-frame, on a piece of thick paper, and loaded as before with the steel roller 2 millim. in diameter.

Nicols crossed and at 45° to the axis of the beam.

The screw load was applied until six interference-fringes appeared under the roller; these were examined through a microscope with a micrometer-eyepiece divided to thousandths of an inch. Light from a sodium-flame was used, and the distance between the point of contact and the intersection of each fringe with the normal was measured in micrometer-divisions.

I. Distances in micrometer-divisions to successive fringes:

11·0 13·5 17·0 23·0 35·0 71·5,

but the shears are as 6 . 5 . 4 . 3 . 2 . 1, since there is a difference of phase of only $\frac{1}{2}$ a wave-length required to produce a fringe, hence taking the products of distances into shears we get

66·0 67·5 68·0 69·0 70·0 71·5.

But we have so far neglected the value of θ, the distance of the axis of shears from the point of contact.

By taking the two most reliable observations, where the distance from the point of contact is large and yet where the fringes are well defined, we should have, if the law is hyperbolic,

$$3(23+\theta)=4(17+\theta),$$

or

$$\theta=1^{*}.$$

Correcting the original readings by adding θ to each, we get

12 14·5 18 24 36 72·5,

and the products become

72 72·5 72 72 72 72·5.

II. Same beam, &c., as before, roller and load readjusted. Distance to successive fringes:—

11·5 14·25 17·75 24·0 36·0 75·0

* One micrometer-division = 0·044 millim.

To find θ, take

$$3(24+\theta)=4(17{\cdot}75+\theta), \text{ or } \theta=1.$$

Correcting the distances, we have

12·5 15·25 18·75 25·0 37·0 76·0,

and the products of the distances into the shears become

75·0 76·25 75·0 75·0 74·0 76·0.

III. Same beam, &c., as before, roller and load readjusted. Distance to successive fringes :—

10·75 12·5 15·25 19·25 26·0 39·0 80·5.

To find θ take $3(26+\theta)=4(19{\cdot}25+\theta)$, whence $\theta=1$.

Correcting the distances, we have

11·75 13·5 16·25 20·25 27·0 40·0 81·5,

and the products become

82·25 81·0 81·25 81·0 81·0 80·0 81·5.

The law of variation of shear along the normal is thus shown to be hyperbolic.

Experiment 3. The steel straining-frame was removed from the instrument and—by a screw inserted in the place of the straining-screw—hung from a balance, which could be loaded with shot and had a leverage of 50 to 1 : a steel stirrup was hung over the frame with two hardened points resting on the two guiding-pins ; one lower end of the stirrup was secured to the body of the balance, the beam inserted and balanced, and shot put in the pan. This lifted the straining-frame and loaded the beam.

Beam [B] 56 millim. × 20 millim. × 6·5 millim. placed on the base of the steel frame on a piece of thin paper : loaded by a steel roller 2 millim. in diameter. Viewed through nicols crossed and at 45° to the horizontal axis of the beam.

The balance was loaded until the first blue fringe was brought down to a given position on the beam, and the weight of shot observed ; the same fringe was then brought down to a lower given position, and the weight of shot again observed, and so on for successive points.

Distance (α) of given points on normal from top of beam, in millim.	Load (β) on roller (weight of shot) $\times$ 50 in lb.			β/α.
	1.	2.	Mean.	
1·15	40	39	39·5	34·34
3·2	114	105	109·5	34·22
4·2	145	149	147	35·00
5·2	182	180	181	34·80
6·2	218	.....	218	35·16

If the shear at 4·2 millim. with 147 lb. be taken as unity, the shear at 5·2 millim. with this same load will be $\frac{147}{181}$, since the same shear is produced at 5·2 millim. with 181 lb. as is produced at 4·2 millim. with 147 lb. Hence if the curve of loading is an hyperbola, we should have

$$4{\cdot}2 \times 1 = \frac{147}{181} \times 5{\cdot}2 \text{ or } \beta/\alpha \text{ a constant.}$$

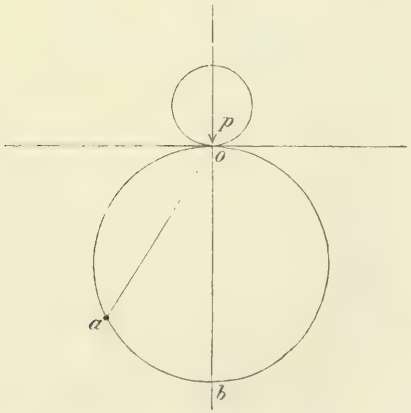
From the third column given above the values of β/α will be seen to be nearly equal in each case; the value of θ has here been neglected; if we put $\theta = 0{\cdot}04$ millim., the values of β/α become

34·6 33·8 34·7 34·5 34·9.

Proposition II.

Things being arranged as in Proposition I., it is required to

Fig. 2.



determine the locus of points of equal intensity of shear, and

to show that at any point whatever the shear is inversely proportional to its distance from the point of contact.

Experiment 4. The beam was examined under circularly polarized light, as in Clerk-Maxwell's experiments, in order to obtain the variations in the amount of the strain uncomplicated by variations in the directions of the principal stress-axes; white light was used.

The loci of points of equal shear were found to be circles, as in the figure; circles of equal shear were obtained up to 8 millim. diameter with this beam.

Hence the shear at any point a equals the shear at b, if $o\,b\,a$ is a circle, and $o\,b$ the normal at o; *i.e.* shear at a

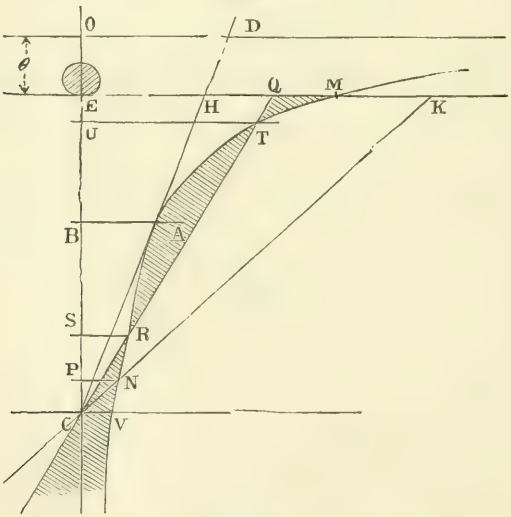
$$= k\frac{p}{ob} = k\frac{p\cos\theta}{oa},$$

k being some constant, but $p\cos\theta$ is the resolved part of the pressure at o* along $o\,a$; hence the shear at any point is inversely proportional to its distance from the point of contact.

Proposition III.

The state of strain at the centre of the beam when doubly supported may be found by superposing on the state of strain

Fig. 3.



due to bending only, that due to surface-loading without bending.

* See Professor Boussinesq's results quoted already.

It has been proved that the state of strain along the normal at the point of contact due to the surface-loading may be represented by an hyperbola whose asymptotes are respectively the normal itself and a line parallel to the axis of the beam at a distance θ from the point of contact. Let O C, O D in fig. 3 represent these asymptotes, O E $=\theta$; let an hyperbola be drawn whose ordinates parallel to O D represent the shear at any point along E C for a given load : since the shear is proportional to the compressive stress, these ordinates may be considered as proportional to the compressive stress at any point along E C.

By our (α) assumption we may represent the stresses at any point along E C, due to bending, by a right line drawn through C, the centre of the depth.

Let C K be such a line, drawn on the same scale as the hyperbola, so that E K represents the shear (vertical stretch) at E due to bending *, while E M represents the shear (vertical squeeze) due to loading.

These two curves must intersect at some point N ; at the corresponding point P on the normal the shear (vertical squeeze) due to the loading is equal to the shear (vertical stretch) due to the bending : an element of volume at P will therefore be subject to voluminal compression only, and the shear will be zero, there will therefore be no birefringent action, and when viewed with crossed nicols there should be a dark spot on a white field.

If the load is kept constant and the span diminished, E K will decrease until C K cuts the hyperbola at a second point ; we should now get two points of darkness. As the span is still diminished these dark points should rise and fall respectively until they coincide, when C K is a tangent to the hyperbola ; after this they should separate out at right angles.

Plate II. fig. 2 gives the results of an experiment (5) made with constant load and varying spans. The beam was 128 millim. × 19 millim. deep × 5·5 millim. thick, supported on two steel rollers 2 millim. in diameter and centrally loaded over a similar roller : the nicols were crossed and at 45° to the axis. The following table gives the spans :—

* The compressive stress due to bending, at any point on C E, produces a shear (vertical stretch) and a voluminal compression, and both are proportional to the stress, similarly for the shear (vertical squeeze) and voluminal compression produced by the stress due to the loading ; so for this purpose it is indifferent whether the ordinates of the two curves represent the compressive stresses or the shears produced.

Curve.	Span in millim.	Ratio of span to depth.
1	120	6·31
2	100	5·26
3	88	4·63
4	80	4·21
5	78	4·10
6	72	3·79

This experiment shows that there are, generally, two points of zero shear which close up as the span diminishes and then open at right angles.

The same phenomena may be observed by placing a beam on a flat surface and loading it, and then placing over this beam a second, which may be bent with a very long span, or by two couples at the end; the effect is the same for different degrees of bending as for varying spans in the former experiment.

Thus for spans of four to five depths the normal under the load is divided into three parts by two points of zero shear, elements between these points being subject to shear (vertical stretch), while elements above and below them are subject to shear (vertical squeeze).

When, however, the span is less than four depths, every element in the cross section under the load is subject to shear (vertical squeeze) and the greatest strained element is immediately under the load.

These results may be further checked and confirmed by examining each part of the normal by placing over it a beam bent in the hand; if the part under examination is in shear, say (vertical squeeze), darkness may be produced by superposing a part of the second beam oppositely strained; if the strains were similar, increased brightness would result.

I exhibit also the results of experiments made to determine the position of the black bands for lower ratios of span to depth.

The dimensions of the beam were 124 millim. × 20 millim. deep × 6·5 millim. thick, loaded on rollers like the others; nicols crossed and at 45° to the axis.

Here the effect of the supports is very marked, so that when $p=2$ the black band only just touches the axis.

It must be remembered that at the point where the black band cuts the normal the shear is zero, but that everywhere else on the band all that is indicated is that the directions of resultant tension and compression are at 45° to the axis of the beam.

Experiment 6 was made to establish Proposition III. with greater certainty.

Beam 128 millim. × 19 millim. × 5·5 millim. was placed on the base of the straining-frame, on a piece of thin paper, and loaded with shot until the first blue fringe came down to a point 1·7 millim. from the top. The load was 65 lb.

The same beam was then supported on two steel rollers 2 millim. in diameter and 120 millim. apart, and centrally loaded over a similar roller until the same blue fringe appeared at the bottom of the beam. The load was 55 lb.

An hyperbola has been drawn (see fig. 1, Plate II.) of convenient proportions, cutting the horizontal through the above-mentioned point at 28·5 divisions from the normal; the shear corresponding to the blue fringe is thus represented by 28·5 divisions, and there is that shear at the point with a load of 65 lb.

Now the stress due to bending, at the extreme bottom fibre of a beam 19 millim. deep, 120 millim. span, and 5·5 millim. thick, with a load of 55 lb., is 1·436 tons per square inch.

The vertical compressive stress at this point, due to the load of 55 lb., is, as is shown later on, 0·121 ton per square inch; but we are not justified in superposing the shears produced by these two stresses, being tensile and compressive at right angles, and the former as much as twelve times the latter, so I shall take the stress at the blue fringe as 1·436 tons per square inch.

Hence the compressive stress produced by 65 lb. over a span of 120 millim., at the top fibre, is

$$1{\cdot}436 \times \frac{65}{55},$$

and the corresponding value in scale-divisions is

$$1{\cdot}436 \times \frac{65}{55} \times \frac{28{\cdot}5}{1{\cdot}436} = 33{\cdot}7 \text{ divisions.}$$

This distance is set off along the top surface in the figure, and the point so found joined to the centre of the middle section: where it cuts the hyperbola we should get darkness on the normal with a span of 120 millim. We can also draw lines representing the bending-stresses for other spans for the same load of 65 lb.

The position of the black bands on the normal, as found by experiment for spans of 120 and 100 millim., are indicated on the normal, and will be found to agree very closely with those points found independently by the intersection of the two curves.

The curve of bending-stresses is a tangent to the curve of loading at a span of 73 millim., as measured from the figure, whereas it is apparently 82 millim. when actually observed ; it would appear more correct to determine this span by drawing the curve through two points which can be observed with accuracy, and then drawing the tangent and measuring the intercept, since the experimental determination of the span giving coincidence of the two dark bands is one liable to considerable error.

By drawing lines from the centre to the points along the top surface corresponding to longer spans we see that the deviation of the so-called "neutral axis" from the centre is considerable : thus even at a span = 10 depths = 190 millim. it should be 1 millim. above the centre.

Proposition IV.

The strain at every point along the normal due to loading varies directly as the load.

Experiment 7. The beam is placed on two supports as before, with a small central load, and the points of intersection of the black bands with the normal are noted. The load is now increased up to the safe limit when the points of intersection are observed to remain unaltered.

We know that the strain at any point on the normal due to bending is proportional to the load ; hence if the point of intersection of the curves of bending and loading remains the same when the load is increased, we know that the strain at any point due to the loading must vary as the load.

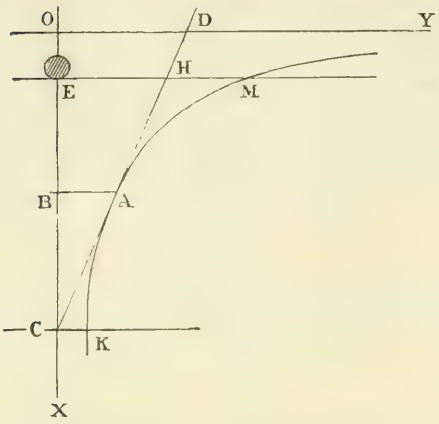
Proposition V.

To determine the constant in the equation to the curve of loading along the normal for any beam.

Let O X represent the vertical through the centre of a beam centrally loaded, E the point of contact of the load with the top of the beam E K ; O Y the axis of shear, $OE=\theta$; K A M the hyperbola of loading for any given load, C A H D the line of stresses due to bending along C E, for the same load, the span being chosen so that C A H is a tangent to the hyperbola at A ; *i. e.* so that the dark bands coincide at B. Then O Y and O X are the asymptotes of the hyperbola.

It has been proved that the equation is of the form $y=k\frac{1}{x}$, where y is the compressive stress at a point on the normal E C at a distance X from O. If W is the load and b

Fig. 4.



the width of the beam = length of bearing of loaded roller, we have

$$y = k \cdot \frac{W}{bx} \text{ —for the given beam.}$$

Then $OD = BA = 2k\frac{W}{bx}$ (since BA represents the stress at B due to the load W). Also $EH = \frac{3}{2}\frac{Wl}{h^2b}$, where EH represents the stress at E due to a load W on a beam of depth h and width b and span l; and

$$\frac{EH}{OD} = \frac{CE}{CO}; \quad \therefore CO = CE\,\frac{OD}{EH},$$

$$\text{or } \frac{h}{2} + \theta = \frac{h}{2} \times 2k\frac{W}{bx} \times \frac{2}{3}\frac{h^2b}{Wl} = \frac{2}{3} \cdot \frac{h^3k}{lx}$$

$$= \frac{2}{3}\,\frac{h^3k}{\frac{l}{2}\left(\frac{h}{2} + \theta\right)} \quad [\text{since } x = \tfrac{1}{2}CO];$$

$$\therefore \left(\frac{h}{2} + \theta\right)^2 = \frac{4}{3}\frac{h^3k}{l};$$

$$\therefore \quad \frac{1}{4} + \frac{\theta}{h} + \frac{\theta^2}{h^2} = \frac{4}{3} \cdot \frac{h}{l} \cdot k; \quad \text{put } \frac{l}{h} = \rho;$$

$$\therefore \quad k = \frac{3}{4}\rho\left(\frac{1}{4} + \frac{\theta}{h} + \frac{\theta^2}{h^2}\right).$$

To find k the beam is placed on two supports and centrally loaded; the two points where the black bands cross the normal are observed (the span being longer than four depths), and plotted, and an hyperbola drawn through them; a tangent is then drawn to this curve from the centre of the section and its intercept on the upper edge measured, the span giving coincidence of the black bands can then be calculated.

Experiment 8. For a beam 128 millim. × 19 millim. deep × 5·5 millim. I find this span to be 73 millim.; hence

$$\rho = \frac{73}{19} = 3{\cdot}84.$$

Taking θ at 0·04 millim., $\frac{\theta}{h} = 0{\cdot}002$ millim., and neglecting $\frac{\theta^2}{h^2}$, we have

$$h = \tfrac{3}{4} \times 3{\cdot}84 \times 0{\cdot}252 = 0{\cdot}726.$$

Proposition VI.

To verify the equation to the curve of loading.

Experiment 9. Beam 128 millim. × 19 millim. × 5·5 millim.

The stress corresponding to the blue fringe with this beam was found, as already explained, by loading the beam over a span of 120 millim., until the blue fringe appeared at the bottom of the beam; the load required was 55 lb.; hence the corresponding stress is 1·436 tons per square inch*.

When laid on the base of the steel frame, the same fringe was observed at 1·7 millim. from the top with a load of 65 lb.

From the equation to the curve of loading, taking $k = 0{\cdot}726$, $\theta = 0{\cdot}04$ millim., we ought to have a stress at 1·7 millim. from the top equal to

$$y = 0{\cdot}726 \times \frac{25{\cdot}4^2}{2240} \times \frac{65}{1{\cdot}74} \times \frac{1}{5{\cdot}5} = 1{\cdot}419 \text{ tons per square inch.}$$

The lines of Principal Stress afford a convenient means of studying the condition of strain in a bent beam.

In a memoir published in 1838† Lamé discussed the

* From the equation $y = k \frac{W}{bx}$, there is a compressive stress of 0·121 ton per square inch here due to the load. I have not added the effect of this to that of the bending, as there is no proof that the superposition of small strains holds when the strains themselves are so unequal.

† *Comptes Rendus*, vol. vii. p. 778: "Mémoire sur les surfaces isostatiques dans les corps solides en équilibre d'élasticité."

problem of the equilibrium of an elastic solid, and investigated the properties of what he termed "isostatic surfaces," or surfaces where only normal "actions" are applied.

In 1870 Saint-Venant* examined the differential equations to which the subject of "isostatic surfaces" gave rise, and in 1872 Professor Boussinesq† gave a geometric method for constructing isostatic lines passing through any given point. This memoir was shortly followed by a second‡, treating of the integration of the equations involved.

Rankine has examined the form of the curves of Principal Stress, and given an expression from which the curves can be drawn§. He neglects the surface-loading effect as "in most cases practically of small intensity when compared with the other elements of stress." On comparing his curves with those in Plate II. it will be noticed how closely the curves of tension agree, while the curves of compression are very dissimilar.

Sir George Airy has calculated and drawn the curves of principal stress for several cases of flexure, including that of a beam doubly supported and centrally loaded‖. He assumes "that there is a neutral point in the centre of the depth; that on the upper side of this neutral point the forces are forces of tension, and on the lower side are forces of compression, and that these forces are proportional to the distances from the neutral point;" but he says "These suppositions seem to imply that the actual extensions or compressions correspond exactly to the curvature of the edge of the lamina." The surface-loading effect is not here taken into account; and it would have been interesting to compare the results as shown in fig. 6, for a beam in which the span equals ten depths, with the actual curve as found by experiment. This comparison, however, would lead to erroneous conclusions, since it has been shown¶ that the results arrived at are not consistent with the fundamental equations, and the form of the curves can be accepted only as a very general approximation.

Proposition VII.

To determine the lines of Principal Stress in a glass beam doubly supported and centrally loaded.

Experiment 10.—A glass beam, 128 millim. × 19 millim.

* Ibid. vol. lxx. † Ibid. vol. lxxiv. p. 242. ‡ Ibid. vol. lxxiv. p. 318.
§ 'Applied Mechanics,' §§ 310 and 311.
‖ Phil. Trans. 1863, part 1.
¶ See criticism on Sir George Airy's solution in Ibbetson's 'Mathematical Theory of Elasticity,' note on p. 358.

deep × 5·5 millim. thick, was placed in the steel straining-frame on two steel rollers 2 millim. in diameter, and centrally loaded over a similar steel roller.

The span chosen was 60 millim., giving for ρ the value 3·15.

The nicols were crossed and set at an observed angle, and the black band plotted on squared paper corresponding to the squares on the glass beam. This band of course represents the locus of points where the axes of principal stress are parallel to the directions of the planes of the nicol.

The nicols were then turned through a small angle α, the new position of the black bands plotted, and so on for several different angles. These curves are shown in Plate II. The lines of principal stress are easily deduced from these and are shown in Plate II. fig. 4.

Since communicating the above, Sir George Stokes has gone very fully into this problem, and has kindly allowed me to quote the following extracts from letters I have received from him on the subject :—

"Let A be the point in the upper surface where the pressure (P) is applied ; B, C the points of support below, which I suppose to be equidistant from A ; D the middle point of BC. Let y be measured downwards from A ; denote BD or DC by a, and AB by b. You have the expressions for the stresses produced by P in an infinite solid $\left(x=\frac{2\mathrm{P}}{\pi}\cdot\frac{1}{y}\right)$, and the question is, What system must we superpose on this to pass to the actual case? This, as I showed you, is the system of stresses produced by a system of forces applied to the surface. The forces consist—(1) of the two pressures $\frac{1}{2}$P at B and C ; (2) of a continuous oblique tension below, represented in drawing by a fan of tensions directed at every point of the lower surface from the point A.

"Imagine now the beam cut into two by a plane along A D. Consider one half only, say that on the B side. Everything will remain the same as before, provided we supply to the surface A D forces representing the pressures or tensions which existed in the undivided beam. On account of the symmetry, the direction of these must be normal.

"At D the vertical pressure on a horizontal plane in the infinite solid is compounded with an equal vertical tension due to the fan. Hence, of the vertical pressure in A D which must be superposed on the vertical pressure in the infinite solid, we know thus much without obtaining a complete solusion of the problem, namely, that it must equal minus $2\mathrm{P}/\pi b$

at D and 0 at A. If we suppose it to vary uniformly between, we are not likely to be far wrong.

"This leads to the following expression for the vertical pressure in A D :—

$$\frac{2P}{\pi}\left(\frac{1}{y}-\frac{y}{b^2}\right).$$

"Now for the horizontal. We know that the complete system of external forces must satisfy the conditions of equilibrium of a rigid body. The direction in each element of the fan passes through A, about which therefore the fan has no moment. Hence the moment of the horizontal forces along A D taken about A must equal $\frac{1}{2}Pa$. Again, the resultant of the semi-fan is a force passing through A, and its vertical component is $\frac{1}{2}P$. Its horizontal component is the integral of

$$\frac{2Pb^2}{\pi}\cdot\frac{x\,dn}{(b^2+x^2)^2},$$

taken from 0 to infinity, or $\frac{P}{\pi}$.

"Hence of the horizontal forces along A D we know these two things :—

(1) The sum must equal $\frac{P}{\pi}$,

(2) The moment round A must equal $\frac{1}{2}Pa$.

"In default of a knowledge of the law according to which the force varies with y, it is natural to take it, for a more or less close approximation, to be expressed by the linear function $A+By$, or say Y. To determine the arbitrary constants A, B, we have only to equate the integral of $Y\,.\,dy$ to $\frac{P}{\pi}$, and that of $Yy\,.\,dy$ to $\frac{1}{2}Pa$, the limits being 0 to b. We thus get for the expression for the tension at any point of A D,

$$\frac{P}{b}\left(\frac{4}{\pi}-\frac{3a}{b}\right)+\frac{6P}{b}\left(\frac{a}{b}-\frac{1}{\pi}\right)\frac{y}{b}.$$

"At neutral points the vertical pressure equals minus the horizontal tension, giving

$$\left(\frac{6\pi a}{b}-8\right)\frac{y^2}{b^2}+\left(4-\frac{3\pi a}{b}\right)\frac{y}{b}+2=0\,;$$

or, putting for shortness $\frac{3\pi a}{b}-4=m$,

$$2m\left(\frac{y}{b}\right)^2 - m\frac{y}{b} + 2 = 0, \quad \therefore \frac{y}{b} = \frac{1}{4} \pm \sqrt{\frac{1}{16} - \frac{1}{m}}.$$

For the neutral points to be real and different, we must have

$$m > 16, \quad \frac{2a}{b} > \frac{40}{3\pi}.$$

When the neutral points coalesce into one, we have m equal 16, y equal $\frac{b}{4}$; and for the ratio of the span to the depth, $\frac{2a}{b}$ equal $\frac{40}{3\pi}$, equal 4·245, or, say, the span is $4\frac{1}{4}$ times the depth.

"As regards the horizontal tension at points along A D, you take a linear function of y as I do, and your condition of moments is the same as my (2), but in lieu of my (1) you do what is equivalent to taking the total tension *nil*. You further omit the correction to the vertical pressure when we pass from a solid of infinite depth to one terminated by a plane below. You further take the coefficient of $\frac{P}{y}$ as k, a constant to be determined by the observations, instead of $\frac{2}{\pi}$.

"Taking the place of the neutral point (at one fourth of the depth) and the ratio of span to depth as given by my formulæ, and then treating them as if they had been the results of experiment, and substituting in your formulæ for the determination of k, I got 0·7947 instead of 0·64. The largeness of your coefficient is I think fully accounted for by the employment of the formulæ which you used.

"In your method you take the stress belonging to the solid supposed infinitely deep, and superpose it on the stress corresponding to a pure bend.

"This comes to the same thing as retaining three terms only in the equation I gave in my letter for determining the y of the neutral points.

"The equation thus becomes

$$\frac{6\pi a}{b} \cdot \frac{y^2}{b^2} - \frac{3\pi a}{b} \cdot \frac{y}{b} + 2 = 0,$$

or

$$2m\frac{y^2}{b^2} - m\frac{y}{b} + 2 = 0,$$

where

$$m = \frac{3\pi a}{b} \text{ instead of } \frac{3\pi a}{b} - 4.$$

"When the two neutral points merge into one, we have in both cases alike y equal $\frac{1}{4}\ b$, and the only difference is that $3\pi\frac{a}{b}$ equals m instead of m plus 4.

"If you had supposed the coefficient for the infinite solid to be an unknown quantity k, and had applied your observations to determine it, using my formulæ instead of your own, you would have got something very close indeed to 0·64.

"It is noteworthy that in your problem, taken as one in two dimensions, the theoretical stresses in the planes of displacement are independent of the ratio between the two elastic constants; in other words, independent of the value of Poisson's ratio."

I have calculated the positions of the neutral points from Sir George Stokes's formula

$$\frac{y}{b} = \frac{1}{4} \pm \sqrt{\frac{1}{16} - \frac{1}{m}}$$

for spans of 88, 100, and 120 millim. in a beam 128 millim. long × 5·5 millim. wide × 19 millim. deep. These are given in the following Table in the 2nd and 3rd columns. The results of actual observations (see p. 494) are given in columns 4 and 5; while columns 6 and 7 give the same points as found by plotting the intersection of the curves of pure bending and loading (infinite solid assumed) :—

Span.	Distance of Neutral Points from top edge, by					
	Sir George Stokes's formula.		Observation.		Intersection of curves.	
88.....	6·3	3·2	6·4	3·3	6·9	2·7
100.....	7·0	2·5	7·2	2·5	7·3	2·3
120.....	7·7	1·8	7·8	1·8	7·8	1·75

The error by the intersection method is greater in proportion as the span is smaller, as might have been expected.

If the observed positions of the neutral points are inserted in Sir George Stokes's formula, the value 0·64 is obtained for the constant k in the equation $x = \frac{2P}{\pi} \cdot \frac{1}{y}$.

M'Gill University, Montreal,
October 12, 1891.

PM 32 (1891)

LXI. *Damping of Electrical Oscillations on Iron Wires.* By John Trowbridge*.

IT has generally been assumed by those who have studied the subject of very rapid oscillations of Electricity, such as occur in Leyden-jar discharges, that the magnetic character of the conductor has very little influence upon the character of the discharge. Thus, in a note to an article on Electrical Waves (*Annalen der Physik und Chemie*, vol. cviii. 1859, p. 499), W. Feddersen states that electrical oscillations may suffer a slight weakening on iron ; but this diminution is very slight, and results from the resistance of iron being greater than that of other metals†.

In Dr. Lodge's treatise on Modern Views of Electricity (ed. 1889) we find the following :—

"But in the case of the discharge of a Leyden jar iron is of no advantage. The current oscillates so quickly that any iron introduced into its circuit, however subdivided into thin wires it may be, is protected from magnetism by inverse currents induced in its outer skin, and accordingly does not get magnetized ; and so far from increasing the inductance of the discharge-circuit, it positively diminishes it by the reaction-effect of these induced currents ; it acts, in fact, much as a mass of copper might be expected to do" (p. 365).

Fleming writes as follows :—

"With respect to the apparent superiority of iron, it would naturally be supposed that since the magnetic permeability of iron bestows upon it greater inductance, it would form a less suitable conductor for discharging with great suddenness electric energy. Owing to the fact that the current only penetrates just into the skin of the conductor, there is but little of the mass of the iron magnetized. Even if these instantaneous discharges are capable of magnetizing iron, ... the electromotive impulses or sudden rushes of electricity do not magnetize the iron, and hence do not find in it any greater self-inductive opposition than they would find in a non-magnetic but otherwise similar conductor. Dr. Lodge's further researches seem to show that there is a real advantage in using iron for lightning-conductors over copper, and that its greater specific resistance and higher fusing-point enable an iron rod or tape to get rid safely of an amount of electric energy

* From an advance proof communicated by the Author.

† "Beim Eisen könnte in Folge der Magnetisirungen eine Abweichung hervortreten ; indess zeigt der Versuch, dass dieselbe keinenfalls bedeutend ist, übrigens in dem Sinne erfolgen müsste, als wenn die Elektricität beim Eisen ein grösseres Hinderniss fände, wie bei den übrigen Metallen."

stored up in the dielectric, which would not be the case if it were copper."*

"In the experiments on alternative path," as described by Dr. Lodge, "the main result is very briefly summed up by saying that, where a sudden discharge had to pass through a conductor, it was found that iron and copper acted about equally well, and indeed iron sometimes exhibited a little superiority, and that the thickness of the conductor and its ordinary conductivity mattered very little indeed. In the case of enormously rapid oscillations the value of the impulsive impedance varies in simple proportion to the frequency of the oscillations, and depends on the form and size of the circuit, but not at all on its specific resistance, magnetic permeability, or diameter. . . . . For discharges of a million per second and upwards, such as occur in jar-discharges and perhaps in lightning, the impedance of all reasonably conducting circuits is the same, and independent of conductivity and permeability, and hardly affected by enormous changes in diameter"†.

Turning now to the observations of Hertz, we find it stated that the material, resistance, and diameter of the wire of the micrometer-circuit employed by him have very little influence on the result. The rate of propagation of an electrical disturbance along a conductor depends mainly on its capacity and coefficient of self-induction, and only to a small extent on its resistance. Hertz concludes that, owing to the great rapidity of the alternations, the magnetism of the iron is unable to follow them and therefore has no effect on the self-induction. When a portion of the micrometer-circuit employed by Hertz was surrounded by an iron tube, or replaced by an iron wire, no perceptible effect was obtained; and thus the result was apparently confirmed that the magnetism of the iron is unable to follow such rapid oscillations and therefore exerts no appreciable effect. The velocity of propagation in a wire has a definite value independent of its dimensions and material. Even iron wires offer no exception to this, showing that the magnetic susceptibility of iron does not play any part in the case of such rapid motions‡.

* Fleming's 'The Induction of Electric Currents,' p. 398. The author describes in full Dr. Lodge's experiments to prove the nonmagnetizability of iron by sudden discharges.

† Fleming, 'The Induction of Electric Currents,' p. 411.

‡ "Ersetzen wir den bisherigen Kupferdraht durch einen dickeren oder dünneren Kupferdraht oder durch einen Draht aus anderem Metall, so behalten die Knoten-punkte ihre Lage bei. Die Fortpflanzungsgeschwindigkeit in allen solchen Drähten ist daher gleich, und wir sind berechtigt von derselben als einer bestimmten Geschwindigkeit zu

Although the impulsive impedance is apparently not affected by the magnetic character of the wire, our experiments lead us to believe that discharges of the quick period of a Leyden jar are affected very appreciably by the magnetic nature of iron, steel, and nickel conductors. This effect is so great that it damps the electrical oscillations, and makes it difficult to determine whether the time of oscillation is also affected by the permeability of the conductor.

The apparatus employed was similar to that described in my investigations of electrical oscillations with an air-condenser (Proc. American Academy of Arts and Sciences, May 28, 1890). Certain important modifications, however, were made. The plane mirror which I used in the former research was replaced by a concave mirror of 10-feet focus and $3\frac{1}{2}$ inches in radius. This mirror was mounted upon the end of the armature-shaft of a one-half horse-power electric motor.

The discharging apparatus consisted of a sharp cutting-tool, insulated, and mounted on the edge of the rotating disk bearing the mirror. It was metallically connected with a grooved ring of brass mounted upon the shaft and insulated from it by hard rubber. Around this was wound a copper wire, one end of which was connected with the discharging wire and the other drawn taut by a rubber band. The electrical discharge was thrown upon the circuit by pushing forward a lever, which brought a solid hinged frame containing a strip of soft type-metal into contact with the rapidly revolving steel cutting-tool. An electrical contact was thus insured by the tool cutting a groove in the strip of type-metal. In order to avoid a spark at the contact, the type-metal was thickly covered with a wax of peculiar composition. The only spark therefore that occurred was the one the oscillations of which I desired to study. At each trial the type-metal was moved so as to expose a new cutting surface. The type-metal was insulated from the rest of the apparatus but connected with the outer coating of the Leyden jar. First, both terminals of the Holtz machine were thrown off, and immediately after, the cutting-tool, ploughing its way through the type-metal, placed the outer coating of the Leyden jar in circuit with one of the two parallel wires leading to the terminals of the spark. The other wire was permanently in connexion with the inner coating of the jar.

---

reden. Auch Eisendrähte machen keine Ausnahme von der allgemeinen Regel, die Magnetisirbarkeit des Eisens kommt also bei so schnellen Bewegungen nicht in Betracht."—*Ann. der Physik und Chemie*, vol. xxxiv. 1888, p. 558.

Besides the short lead wires above described, the discharging circuit consisted of two parallel wires 30 centim. apart and 510 centim. long. These were the only portions of the apparatus changed during the experiment, and they were replaced by wires of different material and of different size. The other conditions—length of spark, lead wires, and the copper cross-wire connecting the outer ends of the long parallel wires—remained undisturbed throughout the experiment.

The Leyden jar was charged each time as nearly as possible to the same potential, judging by the number of turns given the Holtz machine. It is unfortunate that no more accurate means of measuring it were at hand, although the different negatives showed but slight variation. The capacity of the jar with alternations of this period was 5060 electrostatic units.

I describe the discharging portion of the apparatus minutely, for the success of an investigation of this nature depends upon the suppression of all sparks save that which one wishes to observe, and my method surely and completely accomplished this. The photograph of the spark could thus be made to fall very accurately on the sensitive plate. When one considers that the image of the spark was flying through the air on a circle of ten feet radius with a velocity of a mile a second, it will be seen that an extremely small deviation in the point of contact between the cutting-tool and the type-metal would have thrown the image entirely off the sensitive plate. A singular phenomenon was noticed in this connexion. When a comparatively low potential was used, such as that afforded by the air-condenser used in our previous investigation, the cutting-tool ploughed two or three millimetres along the surface of the type-metal before a spark passed at the point in the circuit where it was desired. With higher potentials this phenomenon was also observed but the extent of cutting was diminished. It is possible that the insulating wax may have melted under the sudden blow of the cutting-tool, and, flowing around it, prevented instant contact. This seems to me improbable, for a deep and clear-cut groove was made in the soft type-metal. Great attention was paid to the solid structure of this contact apparatus. It was entirely separate from the support of the revolving parts and was perfectly steady.

The other end of the armature-shaft was lengthened into a cylindrical chronograph, similar to that described in the article already cited, and its performance left nothing to be desired. A small Ruhmkorf coil excited by two storage cells, and interrupted by a seconds pendulum, gave a record

of the speed of the mirror. The stylus which drew the spiral turns on the barrel of the chronograph was drawn along the barrel by means of a small heavily loaded carriage, which, on being released at the moment the lever arm threw the type-metal in contact with the cutting-tool, descended an inclined plane of adjustable height. A small Toepler Holtz machine charged a large Leyden jar, and it was found to work admirably in all states of the weather.

The apparatus which I have thus described was the result of the experiments of the previous year and worked for months without failure; and the taking of photographs of the oscillating discharge by it became a mere matter of routine.

The following cases were tried :—

(1) When the long parallel wires were of copper (diameter ·087 centim.), the number of double oscillations visible on the negatives averaged quite uniformly 9 or 9·5.

(2) Where the wires were of German silver (diameter ·061 centim.), 3 oscillations were visible.

(3) But when an annealed iron wire (diameter ·087 centim.) was substituted, only the first return oscillation was distinctly visible, with occasionally a trace of the first duplicate discharge.

(4) On substituting fine copper wire (diameter ·027 centim.), 5 complete oscillations were quite uniformly visible.

(5) Fine German silver wire (·029 centim.), nickel wire (·019 centim.)*, soft iron (·027 centim.), and piano steel wire (·027 centim.), gave but faintly the first return discharge after the pilot spark.

The pilot sparks were in all cases strong.

The single return discharge through the iron wire did not admit of measurement sufficiently accurate to furnish any basis for calculation of its self-induction. The time did not apparently differ, if at all, by more than 14 or 15 per cent. Some general reasoning based upon the number of oscillations may be of interest. It must be acknowledged, however, that this reasoning is open to criticism, although it affords the most plausible explanation of the phenomenon. The phenomenon itself is not a doubtful one.

The time of a double oscillation for the large-sized copper wire was ·0000020 sec., for the small copper wire ·0000021 sec. The others, as far as could be determined, did not differ much from these values, and for this purpose either value is sufficiently accurate. Denote by R′ the ohmic resistance of the parallel wires to alternating currents of this periodicity, by R the resistance to steady currents.

* Obtained by the kindness of Joseph Wharton, Esq., of Philadelphia.

$$p = \frac{2\pi}{t} = 3{,}000{,}000 \text{ (practically)}.$$

Taking the cases up in order :—

(1) Large copper wire,

$$R = \cdot 285 \times 10^9,$$

and substituting in Lord Rayleigh's formula

$$R' = \sqrt{\tfrac{1}{2}p}l\mu R,$$

$$R' = \cdot 66 \times 10^9.$$

(2) Large German silver wire,

$$R = 9 \cdot 2 \times 10^9,$$

and substituting in the series

$$R' = R\left(1 + \frac{1}{12}\frac{p^2 l^2 \mu^2}{R^2} - \frac{1}{180}\frac{p^4 l^4 \mu^4}{R^4} + \cdots\right),$$

$$R' = 9 \cdot 2 \times 10^9.$$

(3) Large iron wire,

$$R = 2 \cdot 5 \times 10^9,$$

and if there is a true time lag, as often stated, such as to prevent action of the magnetic property of the iron, and if on this assumption we make $\mu = 1$,

$$R' = 2 \cdot 78 \times 10^9.$$

(4) Fine copper,

$$R = 3 \cdot 3 \times 10^9,$$

$$R' = 3 \cdot 5 \times 10^9.$$

(5) Again, as before, call $\mu = 1$ in iron, nickel, and steel.

The length of these circuits was 7·41 metres, the remainder of the 10·20 metres—2·79 metres—being of copper wire of $R' = \cdot 94$. The value of R' in the separate cases, including in each the resistance ·94 of the copper portion, was as follows :—

Soft iron.....	$15 \cdot 0 \times 10^9$,
Piano-steel...	$20 \cdot 7 \times 10^9$,
Nickel.....	$30 \cdot 6 \times 10^9$,
German silver	$23 \cdot 0 \times 10^9$.

The ratio of the strengths of successive discharges during the oscillation is given by the function

$$\epsilon^{\frac{rT}{2L}},$$

where r is the ohmic resistance, T the time of a double

oscillation, and L the self-induction. The ratio of one discharge to the nth one after it is

$$\epsilon^{n\frac{r\mathrm{T}}{2\mathrm{L}}}.$$

If we assume,—and it is a large assumption, but one which perhaps the result will in some measure justify,—that the ratio of the strength of the first to the strength of the last visible discharge is more or less a constant, we may make use of the above data. Denote $\frac{\mathrm{T}}{2\mathrm{L}}$ by A, and call the unknown resistance of the short connecting lead wires and of the spark x. Then will $r=\mathrm{R}'+x$; n will be the number of complete oscillations visible.

Take cases (1) and (2), large copper and large German silver wires,

$$\begin{aligned}\epsilon^{n_1(\mathrm{R}'_1+x)\mathrm{A}} &= \epsilon^{n_2(\mathrm{R}'_2+x)\mathrm{A}},\\ n_1(\mathrm{R}'_1+x) &= n_2(\mathrm{R}'_2+x),\\ 9{\cdot}5({\cdot}66+x) &= 3(9{\cdot}2+x),\\ x &= 3{\cdot}4 \text{ ohms}.\end{aligned}$$

Taking cases (1) and (4), large copper and small copper, similarly,

$$\begin{aligned}n_1(\mathrm{R}'_1+x) &= n_4(\mathrm{R}'_4+x),\\ 9{\cdot}5({\cdot}66+x) &= 5(3{\cdot}5+x),\\ x &= 2{\cdot}6 \text{ ohms}.\end{aligned}$$

Experiments with other copper wires having R′ equal to 3·4 and 1·27 gave 5 and 8 for the values of n respectively, or $x=2{\cdot}4$ ohms.

The resistance (R′) of the lead wires forming part of x was ·8 ohm, leaving as a possible value for the resistance of the spark about 2 ohms.

If taking this value of x we calculate the value of R′ necessary to damp out the oscillation in one complete double discharge in the case of the large iron wire, we shall have

$$\begin{aligned}9{\cdot}5({\cdot}66+3) &= 1(\mathrm{R}'+3),\\ \mathrm{R}' &= 30 \text{ ohms}.\end{aligned}$$

But neglecting the magnetic property of the iron, its calculated resistance to alternating currents of this periodicity was R′=2·78 ohms. This is obviously inadequate and would point to the conclusion that the oscillation is not, as sometimes stated, too rapid to admit of the magnetic action of the iron.

If we substitute this value R′=30 in the equation

$$\mathrm{R}'=\sqrt{\tfrac{1}{2}\rho l\mu}\mathrm{R},$$

we have for the resulting value of the magnetic permeability

$$\mu = 230.$$

This lies between the limits $\mu=103$ and $\mu=1110$, found by taking the number of oscillations one and a half and one half respectively for the case of the iron wire.

It should be noticed that this estimate of μ necessitates assuming that T and L remain the same within broad limits. Measurements of the single oscillation on the negatives show that this is near enough the case. Part of the more rapid decay of the oscillation in the iron may be well ascribed to the dissipation of energy by hysteresis. While we cannot place much reliance upon an estimate of its value in such a case—its percentage effect probably increasing rapidly with the decay of the spark—it is not difficult to show that its influence may be very great.

There still remains the fact, not generally recognized, that in Leyden-jar discharges through iron wires the magnetic property of the iron has time very materially to modify the character of the spark.

I give an example of the measurement of the half oscillation, which was the only one visible on the photograph of the discharge over iron wires, all the others having been damped or extinguished by the iron, in comparison with the measurement of the similar half oscillation on copper wires of the same diameter as the iron wires. The number of oscillations on the copper wires was from eight to ten. The total duration of the discharge on iron wires was only three millionths of a second, while that on similar copper wires was three hundred-thousandths of a second. A steel wire gave the same results as the annealed iron wires.

	Length of first half oscillation in millimetres.		Length of first half oscillation in millimetres.
Fine Iron Wire.	·23 ·21 ·19 — ·21	Large Iron Wire.	·20 ·20 ·19 — ·19
Fine Copper Wire.	·19 ·20 ·20 — ·19	Large Copper Wire.	·17 ·18 ·20 — ·18

I wish to express my deep obligations to my assistant, Mr. W. C. Sabine, for his valuable suggestions and for his skill in the mechanical details of this investigation.

Conclusions.

1. The magnetic permeability of iron wires exercises an important influence upon the decay of electrical oscillations of high frequency. This influence is so great that the oscillations may be reduced to a half oscillation on a circuit of suitable self-induction and capacity for producing them.

2. It is probable that the time of oscillation on iron wires may be changed. Since I have been able to obtain only a half oscillation on iron wires, I have not been able to state this law definitely.

3. Currents of high frequency, such as are produced in Leyden-jar discharges, therefore magnetize the iron.

Jefferson Physical Laboratory,
Cambridge, U.S.

LXII. *Table of Zonal Spherical Harmonics, calculated by* Messrs. C. E. Holland, P. R. Jones, *and* C. G. Lamb. *With a short Explanation and some Illustrations of its use by* Professor John Perry, *D.Sc., F.R.S.**

[Plate I.]

I HAD intended merely to present to the Society for publication a table of Zonal Spherical Harmonics. But some Members whom I have consulted seem to think that I ought also to give one or two examples of the practical use of such a table. The Members of the Society will, I hope, pardon my putting before them one or two elementary examples.

The use of Spherical Harmonics in the numerical solution of practical problems is almost unknown, I believe, except at the Finsbury Technical College, where, every year, I have been accustomed to make some Electrical Engineering students work a few common examples. My students have for some years been in possession of tables of zonal harmonics, but this year I have thought it well to make the tables more complete and to get them published for the general use of students of practical physics.

I have been told that many of the users of such a table would be glad of a few statements of the general principles underlying its use. For the proofs of these statements readers

* Communicated by the Physical Society: read November 14, 1890.

are referred to Mathematical treatises. Many readers will be satisfied with the treatment of the subject in Mr. Ferrer's excellent treatise, which is, however, written only for beginners.

In problems on Heat Conduction (V being temperature), on Hydrodynamics of incompressible fluids (V being velocity-potential*), in Electrostatics (V being electric potential), in Magnetism (V being magnetic potential), and in many other applications of Physics, we require to find V a function of x, y, z which shall satisfy the equation

$$\frac{d^2V}{dx^2} + \frac{d^2V}{dy^2} + \frac{d^2V}{dz^2} = 0, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or, as it is usually written, $\nabla^2 V = 0$ . . . (1), and which shall also satisfy certain other conditions. Now there are many kinds of function which satisfy equation (1). The definition of a Spherical Harmonic is "a *homogeneous* function of x, y, and z, which satisfies equation (1)."

If such a function can be found, say of the ith degree, and if we divide it by r^{2i+1} where $r^2 = x^2 + y^2 + z^2$, it can be proved that the resulting expression will also satisfy (1), where i may be a positive or negative integer or fraction.

Now if a Spherical Harmonic of degree i (generally called a Solid Spherical Harmonic) be divided by r^i, we get what is called a *Surface* Spherical Harmonic of degree i.

It was shown by Green that if there is a function V which satisfies equation (1) at every point of any given surface, then it is the only function which satisfies (1) throughout space; and there is always a function V obtainable which satisfies (1). It is the characteristic property of a surface spherical harmonic distribution of density of attracting matter on a spherical surface, that it produces a similar and similarly placed spherical harmonic distribution of potential over any concentric spherical surface throughout space, external and internal.

Instead of using x, y, and z coordinates we may of course use r, θ, and ϕ coordinates.

* When there exists a velocity-potential V in a portion of fluid, we mean that the velocity of the fluid at any place resolved in the direction s is

$$-\frac{dV}{ds}.$$

When the motion is "rotational," as in the wheel of a centrifugal pump or turbine, a velocity-potential does not exist. In any portion of a frictionless fluid, if there is irrotationality, that is, if there is a velocity-potential, the property cannot be destroyed.

In a great number of practical cases V is symmetrical about an axis, and a symmetrical spherical harmonic is said to be a Zonal Spherical Harmonic. Taking the axis of symmetry as the axis of z, V is a function of z and $\sqrt{x^2+y^2}$. Or, in polar coordinates, V is a function of r and θ.

Let O be a point in the axis, the origin of coordinates; let the distance of any point P from O be called r, let the angle between O P and the axis be called θ, then in any distribution which has an axis of symmetry we need only to know r and θ. And over any spherical surface whose centre is O, the distribution will be a function of θ. Any zonal surface spherical harmonic is then merely a function of θ, and I give a table of values of these for values of θ differing by 1° from 0° to 90°, up to the harmonic of the seventh degree. These are indicated by P_0, P_1, P_2, &c. P_7.

The surface harmonic of no degree is 1, and is indicated by P_0.

The student is referred to Mathematical treatises for the proof that, if μ be written to represent cos θ, then

$$P_0 = 1,$$

$$P_1 = \mu,$$

$$P_2 = \frac{3\mu^2-1}{2},$$

$$P_3 = \frac{5\mu^3-3\mu}{2},$$

$$P_4 = \frac{35\mu^4-30\mu^2+3}{8},$$

$$P_5 = \frac{63\mu^5-70\mu^3+15\mu}{8},$$

$$P_6 = \frac{231\mu^6-315\mu^4+105\mu^2-5}{16},$$

$$P_7 = \frac{429\mu^7-693\mu^5+315\mu^3-35\mu}{16}.$$

Any function of θ may be expanded in terms of P_0, P_1, P_2, &c., that is any symmetrical function V may be expanded in a series of Zonal Spherical Harmonics. Take, for example, the powers of cos θ, it may be shown that

$$\mu^0 = 1 = P_0,$$

$$\mu = P_1.$$

$$\mu^2 = \frac{2}{3} P_2 + \frac{1}{3} P_0,$$

$$\mu^3 = \frac{2}{5} P_3 + \frac{3}{5} P_1,$$

$$\mu^4 = \frac{8}{35} P_4 + \frac{4}{7} P_2 + \frac{1}{5} P_0,$$

$$\mu^5 = \frac{8}{63} P_5 + \frac{4}{9} P_3 + \frac{3}{7} P_1.$$

And also

$$\text{Cos } \theta = P_1,$$

$$\text{Cos } 2\theta = \frac{4}{3} P_2 - \frac{1}{3} P_0,$$

$$\text{Cos } 3\theta = \frac{8}{5} P_3 - \frac{3}{5} P_1,$$

$$\text{Cos } 4\theta = \frac{64}{35} P_4 - \frac{16}{21} P_2 - \frac{1}{15} P_0,$$

$$\text{Cos } 5\theta = \frac{128}{63} P_5 - \frac{8}{9} P_3 - \frac{1}{7} P.$$

There is an easy rule for expanding any function of θ in terms of P_0, P_1, P_2 &c.

The following table up to P_5 was primarily calculated separately by Messrs. C. E. Holland and P. R. Jones, who checked each other's result by comparison.

Mr. C. G. Lamb applied certain checks to the results of Messrs. Holland and Jones, and then calculated P_6 and P_7.

It is quite easy to extend the table to P_8, for it can be proved that there is a law connecting three consecutive harmonics, say the $(n-2)$th, $(n-1)$th, and the nth.

$$nP_n = (2n-1)\mu P_{n-1} - (n-1) P_{n-2}.$$

θ.	P_1.	P_2.	P_3.	P_4.	P_5.	P_6.	P_7.
°							
0	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
1	·9998	·9995	·9991	·9985	·9977	·9967	·9955
2	·9994	·9982	·9963	·9939	·9909	·9872	·9829
3	·9986	·9959	·9918	·9863	·9795	·9713	·9617
4	·9976	·9927	·9854	·9758	·9638	·9495	·9329
5	·9962	·9886	·9773	·9623	·9437	·9216	·8961
6	·9945	·9836	·9674	·9459	·9194	·8881	·8522
7	·9925	·9777	·9557	·9267	·8911	·8476	·7986
8	·9903	·9709	·9423	·9048	·8589	·8053	·7448
9	·9877	·9633	·9273	·8803	·8232	·7571	·6831
10	·9848	·9548	·9106	·8532	·7840	·7045	·6164
11	·9816	·9454	·8923	·8238	·7417	·6483	·5461
12	·9781	·9352	·8724	·7920	·6966	·5892	·4732
13	·9744	·9241	·8511	·7582	·6489	·5273	·3940
14	·9703	·9122	·8283	·7224	·5990	·4635	·3219
15	·9659	·8995	·8042	·6847	·5471	·3982	·2454
16	·9613	·8860	·7787	·6454	·4937	·3322	·1699
17	·9563	·8718	·7519	·6046	·4391	·2660	·0961
18	·9511	·8568	·7240	·5624	·3836	·2002	·0289
19	·9455	·8410	·6950	·5192	·3276	·1347	−·0143
20	·9397	·8245	·6649	·4750	·2715	·0719	−·1072
21	·9336	·8074	·6338	·4300	·2156	·0107	−·1662
22	·9272	·7895	·6019	·3845	·1602	−·0481	−·2201
23	·9205	·7710	·5692	·3386	·1057	−·1038	−·2681
24	·9135	·7518	·5357	·2926	·0525	−·1559	−·3095
25	·9063	·7321	·5016	·2465	·0009	−·2053	−·3463
26	·8988	·7117	·4670	·2007	−·0489	−·2478	−·3717
27	·8910	·6908	·4319	·1553	−·0964	−·2869	−·3921
28	·8829	·6694	·3964	·1105	−·1415	−·3211	−·4052
29	·8746	·6474	·3607	·0665	−·1839	−·3503	−·4114
30	·8660	·6250	·3248	·0234	−·2233	−·3740	−·4101
31	·8572	·6021	·2887	−·0185	−·2595	−·3924	−·4022
32	·8480	·5788	·2527	−·0591	−·2923	−·4052	−·3876
33	·8387	·5551	·2167	−·0982	−·3216	−·4126	−·3670
34	·8290	·5310	·1809	−·1357	−·3473	−·4148	−·3409
35	·8192	·5065	·1454	−·1714	−·3691	−·4115	−·3096
36	·8090	·4818	·1102	−·2052	−·3871	−·4031	−·2738
37	·7986	·4567	·0755	−·2370	−·4011	−·3898	−·2343
38	·7880	·4314	·0413	−·2666	−·4112	−·3719	−·1918
39	·7771	·4059	·0077	−·2940	−·4174	−·3497	−·1469
40	·7660	·3802	−·0252	−·3190	−·4197	−·3234	−·1003
41	·7547	·3544	−·0574	−·3416	−·4181	−·2938	−·0534
42	·7431	·3284	−·0887	−·3616	−·4128	−·2611	−·0065
43	·7314	·3023	−·1191	−·3791	−·4038	−·2255	·0398
44	·7193	·2762	−·1485	−·3940	−·3914	−·1878	·0846
45	·7071	·2500	−·1768	−·4062	−·3757	−·1485	·1270
46	·6947	·2238	−·2040	−·4158	−·3568	−·1079	·1666
47	·6820	·1977	−·2300	−·4252	−·3350	−·0645	·2054
48	·6691	·1716	−·2547	−·4270	−·3105	−·0251	·2349
49	·6561	·1456	−·2781	−·4286	−·2836	+·0161	·2627
50	·6428	·1198	−·3002	−·4275	−·2545	+·0563	·2854
51	·6293	·0941	−·3209	−·4239	−·2235	+·0954	·3031
52	·6157	·0686	−·3401	−·4178	−·1910	+·1326	·3153
53	·6018	·0433	−·3578	−·4093	−·1571	+·1677	·3221
54	·5878	·0182	−·3740	−·3984	−·1223	+·2002	·3234

Table (*continued*).

θ.	P_1.	P_2.	P_3.	P_4.	P_5.	P_6.	P_7.
55°	·5736	−·0065	−·3886	−·3852	−·0868	+·2297	·3191
56	·5592	−·0310	−·4016	−·3698	−·0510	+·2559	·3095
57	·5446	−·0551	−·4131	−·3524	−·0150	+·2787	·2949
58	·5299	−·0788	−·4229	−·3331	·0206	+·2976	·2752
59	·5150	−·1021	−·4310	−·3119	·0557	+·3125	·2511
60	·5000	−·1250	−·4375	−·2891	·0898	+·3232	·2231
61	·4848	−·1474	−·4423	−·2647	·1229	+·3298	·1916
62	·4695	−·1694	−·4455	−·2390	·1545	+·3321	·1571
63	·4540	−·1908	−·4471	−·2121	·1844	+·3302	·1203
64	·4384	−·2117	−·4470	−·1841	·2123	+·3240	·0818
65	·4226	−·2321	−·4452	−·1552	·2381	+·3138	·0422
66	·4067	−·2518	−·4419	−·1256	·2615	+·2996	·0021
67	·3907	−·2710	−·4370	−·0955	·2824	+·2819	−·0375
68	·3746	−·2896	−·4305	−·0650	·3005	+·2605	−·0763
69	·3584	−·3074	−·4225	−·0344	·3158	+·2361	−·1135
70	·3420	−·3245	−·4130	·0038	·3281	+·2089	−·1485
71	·3256	−·3410	−·4021	·0267	·3373	+·1786	−·1811
72	·3090	−·3568	−·3898	·0568	·3434	+·1472	−·2099
73	·2924	−·3718	−·3761	·0864	·3463	+·1144	−·2347
74	·2756	−·3860	−·3611	·1153	·3461	+·0795	−·2559
75	·2588	−·3995	−·3449	·1434	·3427	+·0431	−·2730
76	·2419	−·4112	−·3275	·1705	·3362	+·0076	−·2848
77	·2250	−·4241	−·3090	·1964	·3267	−·0284	−·2919
78	·2079	−·4352	−·2894	·2211	·3143	−·0644	−·2943
79	·1908	−·4454	−·2688	·2443	·2990	−·0989	−·2913
80	·1736	−·4548	−·2474	·2659	·2810	−·1321	−·2835
81	·1564	−·4633	−·2251	·2859	·2606	−·1635	−·2709
82	·1392	−·4709	−·2020	·3040	·2378	−·1926	−·2536
83	·1219	−·4777	−·1783	·3203	·2129	−·2193	−·2321
84	·1045	−·4836	−·1539	·3345	·1861	−·2431	−·2067
85	·0872	−·4886	−·1291	·3468	·1577	−·2638	−·1779
86	·0698	−·4927	−·1038	·3569	·1278	−·2811	−·1460
87	·0523	−·4959	−·0781	·3648	·0969	−·2947	−·1117
88	·0349	−·4982	−·0522	·3704	·0651	−·3045	−·0735
89	·0175	−·4995	−·0262	·3739	·0327	−·3105	−·0381
90	·0000	−·5000	−·0000	·3750	·0000	−·3125	·0000

N.B.—To find P_i, if θ lies between 90° and 180°, look up the value for the angle $180°-\theta$, and change the sign if i be odd.

When P_1, P_2, &c. are plotted as radial heights and depths above and below a quadrant, the resulting curves, especially if coloured, are exceedingly interesting. A student can draw them to a useful scale in about one hour.

Example I.

The density σ of attracting matter on a spherical shell 1 centim. in radius is proportional to the square of the

distance of any point from a diametral plane, being 6 per square centimetre where greatest: find the potential A inside and B outside. Taking the diametral plane as the equator and θ as the co-latitude, it is obvious that

$$\sigma = 6\mu^2.$$

The expansion of μ^2 in spherical harmonics is already given as

$$\mu^2 = \frac{1}{3}P_0 + \frac{2}{3}P_2.$$

So that we have σ in spherical harmonics,

$$\sigma = 2P_0 + 4P_2.$$

Hence, as A and B are derivable from the same surface harmonics,

$$A = A_0 P_0 + A_2 r^2 P_2,$$

$$B = \frac{B_0}{r} P_0 + \frac{B_2}{r^3} P_2;$$

where A_0, A_2, B_0, B_2 are constants to be found.

Now at the surface, that is where $r=1$, $A=B$, and we can apply this to every harmonic separately. Hence

$$A_0 = B_0, \quad A_2 = B_2.$$

Again, we know from the theory of attraction that the resultant force just outside and just inside the shell differs by the amount $4\pi\sigma$, or

$$\frac{dA}{dr} - \frac{dB}{dr} = 4\pi\sigma ;$$

and this is to be applied to every harmonic separately. Thus, taking terms involving P_0, we have

$$0 + B_0 r^{-2} = 4\pi \times 2 ;$$

or putting $r=1$,

$$B_0 = 8\pi.$$

Again, taking the second terms,

$$2A_2 r + 3B_2 r^{-4} = 4\pi \times 4 ;$$

or, as $A_2 = B_2$, and putting $r=1$,

$$5B_2 = 16\pi, \quad \therefore \ B_2 = \frac{16}{5}\pi.$$

Hence we have

$$\text{Inside potential} \quad A = 8\pi P_0 + \frac{16}{5}\pi r^2 P_2,$$

$$\text{Outside potential} \quad B = \frac{8\pi}{r} P_0 + \frac{16}{5}\pi \frac{1}{r^3} P_2 ;$$

or

$$\frac{A}{8\pi} = P_0 + \frac{2}{5} r^2 P_2 = \alpha \text{ say}, \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{B}{8\pi} = \frac{1}{r} P_0 + \frac{2}{5}\frac{1}{r^3} P_2 = \beta \text{ say}. \quad . \quad . \quad . \quad (2)$$

As, for our purpose, the actual unit of potential is unimportant, we will use α for $\frac{A}{8\pi}$, and β for $\frac{B}{8\pi}$.

I had no notion of how the equipotential surfaces would shape, and I tried to avoid forming any such notion, as it was my object to test the usefulness of the tables in working out any new problem. The first thing that it strikes one to do in this case is to find the potential on the sphere itself. This can be done from either (1) or (2) by putting $r=1$, and then

$$\alpha = P_0 + \frac{2}{5} P_2, \quad \text{or } 1 + \frac{2}{5} P_2.$$

We can now find α for various values of θ, using the table. Thus when $\theta=0$, $P_2=1$, and therefore $\alpha=1{\cdot}4$. Thus we have the following values:—

θ	0	15	30	45	60	75	90
P_2.....	1	·9	·625	·25	−·125	−·3995	−·5000
α	1·4	1·36	1·25	1·1	0·95	0·84	0·80

Next, take any value of θ, say $\theta=45°$. Then from the table, $P_2=0{\cdot}2500$, so that

$$\text{inside}, \quad \alpha = 1 + \frac{1}{10} r^2 ;$$

$$\text{outside}, \beta = \frac{1}{r} + \frac{1}{10}\frac{1}{r^3}, \quad \text{or } \frac{10r^2+1}{10r^3}.$$

For any value of r less than 1 we calculate α; for any value of r greater than 1 we calculate β.

For $\theta=45°$.

r ...	0	·1	·2	·3	·4	·5	·6	·7	·8	·9	1·0
α ...	1	1·001	1·004	1·009	1·016	1·025	1·036	1·049	1·064	1·081	1·100
r ...	1·2	1·4	1·6	1·8	2·0	2·2	2·6	3·0	3·5	4	5
β ...	·8912	·7507	·65	·572	·512	...	...	...	...	...	·2

Now on a sheet of squared paper I plotted the values of r and α or β, and so found the values of r for such particular values of α or β as seemed suitable for curve-drawing. In fact I found the values of r for $\theta=45°$ for various equipotential surfaces.

Repeating this for other values of θ and drawing radial lines on a sheet of paper, it was easy to draw the equipotential surfaces.

The figure (Pl. I.) was obtained in this way by Mr. Joselin. It shows the equipotential surfaces from 0·5 to 1·4. These surfaces are surfaces of revolution. Of course the resultant force anywhere is inversely as the normal distance apart of the equipotential surfaces, and the direction of the force is everywhere normal to the equipotential surfaces.

Example II.

One circular spire of wire of radius a has an electric curtric current C flowing in it. Find the electromagnetic potential everywhere.

At any point on the axis, z centimetres from the centre, the potential is

$$V=2\pi C\left(1-\frac{z}{\sqrt{z^2+a^2}}\right). \quad . \quad . \quad . \quad . \quad (1)$$

It is always worth while at first to get an idea of the range of values of V.

Putting $z=0$, $V=2\pi C$.

$z=a$, $V=\cdot 293\times 2\pi C$.

$z=\infty$, $V=0$.

For the sake of ease of calculation let $2\pi C=1$, and let $a=1$ centim.

Then
$$V=1-\frac{z}{\sqrt{z^2+1}}.$$

We can expand this in powers both of z and of $\frac{1}{z}$, and we have either

$$V=1-z+\frac{1}{2}z^3-\frac{3}{8}z^5+\frac{5}{16}z^7-\frac{35}{128}z^9+\&c. \quad . \quad . \quad (2)$$

or

$$V=\frac{1}{2}\frac{1}{z^2}-\frac{3}{8}\frac{1}{z^4}+\frac{5}{16}\frac{1}{z^6}-\frac{35}{128}\frac{1}{z^8}+\&c. \quad . \quad . \quad . \quad (3)$$

Now, if we can find V as a function of r and θ which is correct along the axial line, then it must be correct everywhere. [This is Green's theorem, assuming that the axial line to infinity is a cylindric surface of no lateral dimensions.] But it is obvious that

$$V=1-rP_1+\frac{1}{2}r^3P_3-\frac{3}{8}r^5P_5+\frac{5}{16}r^7P_7-\frac{35}{128}r^9P_9+\&c. \quad . \quad (4)$$

becomes (2) when $\theta=0$; and

$$V=\frac{1}{2}\frac{P_1}{r^2}-\frac{3}{8}\frac{P_3}{r^4}+\frac{5}{16}\frac{P_5}{r^6}-\frac{35}{128}\frac{P_7}{r^8}+\&c. \quad . \quad . \quad (5)$$

becomes (3) when $\theta=0$.

Hence these express the potential everywhere. The first of these is useful for calculation only when r is less than 1. The second is useful only when r is greater than 1.

And this shows a defect of the Spherical Harmonic method. For if r is nearly 1 we cannot easily calculate V from either of the series, having to use too many terms. It will, however, be found, even in this case, that when we use the harmonics up to P_{11} for any value of θ we can plot V on squared paper from $r=0$ to $r=0{\cdot}9$, and from $r=1{\cdot}1$ to values of r as large as we please. If the intermediate part of the curve from $r=0{\cdot}9$ to $r=1{\cdot}1$ be drawn with a little judgment, it is astonishing how quickly and accurately the equipotential surfaces may be drawn. The result may be compared with the lines of force as worked out by the elliptic integral method of Sir William Thomson.

Any such Electromagnetic solution is also the solution of a Hydrodynamic problem.

The principle adopted in this example is very useful. It is

this :—If the potential at any point along an axis is expressible as

$A_0+A_1z+A_2z^2+$ &c., where A_0, A_1, A_2, &c. are constants, then the potential *anywhere* is

$$A_0P_0+A_1P_1r+A_2P_2r^2+\text{ &c.}$$

If the potential along an axis is

$$\frac{B_0}{z}+\frac{B_1}{z^2}+\frac{B_2}{z^3}+\text{ &c., where } B_0,\ B_1,\ B_2, \text{ &c. are constants,}$$

the potential anywhere is

$$\frac{B_0P_0}{r}+\frac{B_1P_1}{r^2}+\frac{B_2P_2}{r^3}+\text{ &c.}$$

I gave to Mr. Holland, as an example, the case of a hollow cylindric coil of wire, 2 centim. long, 1 centim. in radius inside, and 2 centim. radius outside : to find the magnetic potential everywhere when there are n turns of wire in the coil per unit length of the coil and there is unit current in the wire. Mascart gives for such a case the force at any point of the axis, and it is possible to expand Mascart's expression in powers of z and again in powers of $\frac{1}{z}$; so that it is easy to get the potential in powers of z and of $\frac{1}{z}$, and therefore, as in the last case, the potential everywhere. Now inside the coil and well outside it only a few terms of the series need calculation ; but just at the ends of the coil the calculation is troublesome because many terms are required.

Mr. Holland tried to shorten the work in the following way. He found that the potential at points along the axis could be expressed *approximately* from $z=0$ to $z=2{\cdot}5$, with a maximum error anywhere of only 2 per cent., by

$$V=2\pi n^2(2-{\cdot}4884z+{\cdot}05513z^3-{\cdot}00518z^5+{\cdot}00022z^7),$$

z being measured from the middle point of the coil.

Hence, he said, the magnetic potential at a point r, θ is

$$V=2\pi n^2\{2-{\cdot}4884\,P_1r+{\cdot}05513\,P_3r^3-{\cdot}00518\,P_5r^5+{\cdot}00022\,P_7r^7\}.$$

From this he plotted equipotential surfaces and lines of force. He found that, inside the coil, and indeed everywhere near the coil except certain critical positions, these were approximately correct. But at the flat ends close to the wire they were absurdly wrong. It is easy now to see the physical meaning of Mr. Holland's approximation, and why we cannot use this

ingenious quick way of working ; but we had to be taught by experience.

Example III.

A solid bounded by a surface of revolution moves axially in an infinite mass of incompressible fluid which has no other motion than this gives to it. Find the motion.

In this case

$$\nabla^2 V = 0 :$$

and $-\frac{dV}{dn}$ at any point at the surface of the solid (dn being an element of the normal) in the fluid is really the normal velocity of the solid itself. Again, V must be constant at any infinite distance.

This may easily be worked out for any surface of revolution. Applying it to a sphere of 1 centim. radius. Let v be the velocity of the centre of the sphere in the direction parallel to the axis of z. Then $\frac{dV}{dr} = v\cos\theta$ at any point at the surface of the sphere.

Expressing V in zonal harmonics, and taking it as 0 at an infinite distance,

$$V = \frac{A_0 P_0}{r} + \frac{A_1 P_1}{r^2} + \frac{A_2 P_2}{r} + \&c.$$

$\frac{dV}{dr}$ when $r=1$ is

$$v\cos\theta = -A_0 P_0 - 2A_1 P_1 - 3A_2 P_2 - \&c.$$

But $P_1 = \mu = \cos\theta$, so that the other coefficients vanish, and

$$A = -\frac{v}{2},$$

so that

$$V = -\tfrac{1}{2}\frac{v}{r^2} P_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The equipotential surfaces which a student will draw from (1) are perfectly well known. It is a good exercise to draw them.

If now a velocity $-v$ is impressed upon the whole system, sphere and fluid, we have the case of the sphere at rest and the fluid moving past it. We now merely add the term $-vr\cos\theta$ to (1) and obtain

$$V = -v\left(r + \frac{1}{2r^2}\right) P_1, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which again is easily represented upon paper in equipotential surfaces.

LXIII. *A Kinetic Theory of Solids, with an Experimental Introduction.* *By* William Sutherland.

[Concluded from p. 225.]

Theory.

THE working out of a kinetic theory of solids ought, on purely theoretic grounds, to have proved a simpler matter than that of the kinetic theory of gases, because in solids each molecule abides about a fixed mean position; but the generality of the two great experimental laws of perfect gases stimulated theory to overcome the more difficult task first. The experimental laws which have just been established for solids seem to give as good a guarantee that in its essence the kinetic theory of solids must be as simple a matter as that of gases.

We will therefore start out on the assumption that in solids the molecules have the properties assigned to them in the kinetic theory of gases, that they attract one another, and that each one moves in a small region of space round a certain mean position. In the almost purely statical molecular theories of solids put forth in the early part of this century by the great French elasticians, repulsive forces had to be imagined to equilibrate the attractive; for example, Poisson's molecular theory was founded on the supposition that while molecules of matter attracted molecules of matter, they repelled the particles of heat, so that each molecule was in equilibrium under two sets of opposite central forces. But it is easy to see that no theory founded on purely central attractions and repulsions can explain the facts of rigidity as we actually know them, because in a pure shear, as there is no change of volume, there can be no change in the potential energy of the purely centrally acting molecules; or, more accurately, a small shear of the first order will produce a change of potential energy of the second order of small quantities, but experiment shows that the change of energy in a shear is of the same order of magnitude as the change that accompanies a change of volume: hence purely central attractions and repulsions, while they can give a sort of rigidity, give one infinitely different from that of nature. The statical theory can give equations of the same form as the natural ones, but with some of the coefficients infinitely smaller.

Attempts have been made to avoid this difficulty by giving the molecules polar properties, which, however, can hardly be

got to be compatible with the behaviour of isotropic bodies. The true solution of the difficulty lies in taking account of the kinetics of the molecules. The motion of the molecules is a fundamental part of the phenomenon of elasticity of solids as of gases.

The subject-matter of the kinetic theory of solids will be taken in the following order :—

1. Establishment of the characteristic equations of solids.
2. Testing of the equations on the supposition that the molecules are unalterable.
3. Testing of equations on the supposition that the molecules alter somewhat with change of temperature.
4. Further evidence of the alteration of molecules with change of temperature.
5. Periods of vibration of the molecules of metals.
6. Comparison of the theoretical variation of Young's modulus with temperature with the experimental.
7. Rigidity according to the kinetic theory.
8. Ratio of lateral contraction to elongation in Young's experiment.
9. Dulong and Petit's law, Joule and Kopp's law, and the equation for compound solids.
10. The parameter of molecular force.

1. *Establishment of the characteristic Equations of Solids.*— In the kinetic theory of gases molecules are supposed to exercise pressure on an external body by colliding against its molecules, and the molecules are supposed to collide with one another. Let us imagine, then, a number of molecules of equal mass and size moving amongst one another under the influence of an attractive force $\phi(r)$ exerted by each, and colliding and rebounding with coefficient of restitution unity. If the molecules are close enough together, it is evident that each separate molecule is hemmed in by its neighbours, so that it cannot change its position beyond vibrating about in its own limited share of space which I call its domain. Such a collection of molecules has one characteristic property of a solid body. Liquefaction occurs when each molecule ceases to be hemmed in and just manages to wriggle through amongst its neighbours. In the solid body each molecule as it knocks about in its domain has its mean position preserved, just as if it were held there by central repulsive forces emanating from all the other molecules, or only from its immediate neighbours, while it itself by colliding with its neighbours many times a second in all directions acts virtually as a centre of repulsion to them. There is this much

in common, then, between the kinetic theory and the old static ones, with the great difference, however, that the kinetic state of the molecules is taken account of and regarded as the fundamental cause of the effective repulsions, and these repulsions act only between immediate neighbours, and do not extend to all distances as the attractions do.

What are the conditions of equilibrium in our system of molecules? First, let us take the case of a solid homogeneous and isotropic body free from external force. Suppose it divided into two parts by a plane, and on unit area in the plane suppose a right cylinder erected in one part of the body; this cylinder as a whole is attracted by the half of the body on the other side of the plane, and this attraction can be equilibrated only by the repulsion due to the collisions occurring across the base of the cylinder. Accordingly we must evaluate these two forces. Let the distribution of molecules be a cubical one with edge of cube e; then, in the manner of Poisson (*Journal de l'Ecole Polytech.* Cahier xx.), the attraction on the cylinder is easily proved to be $\frac{1}{6e^3}\Sigma r\phi(r)$, where the summation extends to all molecules within reach of appreciable action of one fixed molecule.

To evaluate the collisional repulsion on the base of the cylinder, we will first take a short cut justified by the theory of gases, and then verify the result by another method. The short cut consists in assuming that the collisional transfer of momentum goes on as if all the molecules had the average velocity square, and as if one third of the number always travelled parallel to each of three rectangular axes. Take one axis to be perpendicular to the unit-base of the cylinder, and let n be the number of molecules per unit area, so that $n=1/e^2$, then $n/3$ molecules collide against the base of the cylinder with velocity v, and the number of times per second that each strikes the base is $v/2\alpha$, where α is the mean swing of a molecule inside its domain. As each molecule has its velocity reversed by a collision, the force of the collisions on the base of the cylinder is $\frac{n}{3}2mv\frac{v}{2\alpha}$ or $mv^2/3e^2\alpha$, and for equilibrium we have the equation

$$\frac{mv^2}{3e^2\alpha}-\frac{1}{6e^3}\Sigma r\phi(r)=0; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or, as we have been dealing with average values, we may as well sum for all the molecules of the body and put our result in the form

$$\Sigma\frac{mv^2}{2\alpha}-\frac{1}{2}\cdot\frac{1}{2}\cdot\frac{1}{e}\Sigma\Sigma r\phi(r)=0. \quad . \quad . \quad (1a)$$

The same equation will now be established from Clausius's equation of the virial, taking account of the virial of the repulsions during collision as Lorentz does (Wied. *Ann.* xii.) in the case of gases. Let F be the repulsive force between two molecules in collision when their centres are distance E apart, then the equation of the virial is

$$\Sigma \frac{1}{t}\int_0^t \frac{mv^2}{2}\,dt$$

$$= \frac{1}{2}\cdot\frac{1}{2}\Sigma\Sigma\frac{1}{t}\int_0^t r\phi(r)\,dt - \frac{1}{2}\cdot\frac{1}{2}\Sigma\frac{1}{t}\int_0^t \mathrm{EF}\,dt + \text{terms}$$

which vanish when the motion is stationary and t is large enough. As E is practically constant during collision,

$$\int \mathrm{EF}\,dt = \mathrm{E}\int \mathrm{F}\,dt.$$

Now suppose each encounter to last a time τ, then, since each molecule in time t experiences vt/α collisions, we have

$$\int_0^t \mathrm{EF}\,dt = \frac{vt\mathrm{E}}{\alpha}\int_0^\tau \mathrm{F}\,dt = \frac{vt\mathrm{E}}{\alpha}\,2mv\,;$$

and then

$$\Sigma\frac{mv^2}{2} = \frac{1}{2}\cdot\frac{1}{2}\Sigma\Sigma r\phi(r) - \frac{1}{2}\cdot\frac{1}{2}\Sigma\frac{2mv^2\mathrm{E}}{\alpha},$$

$$\therefore\ \Sigma\frac{mv^2}{2}\left(1+\frac{\mathrm{E}}{\alpha}\right) = \frac{1}{2}\cdot\frac{1}{2}\Sigma\Sigma r\phi(r).$$

Now E is the mean distance apart of the molecules when in contact, and accordingly

$$\mathrm{E}+\alpha = e\,;$$

hence, as before,

$$\frac{1}{\alpha}\Sigma\frac{mv^2}{2} - \frac{1}{2}\cdot\frac{1}{2}\cdot\frac{1}{e}\Sigma\Sigma r\phi(r) = 0.$$

In the usual theory of gases the molecules are treated as elastic spheres, in which case E is constant; but as change of temperature is known to produce changes inside the molecule, it will be safer to consider E as possibly a function of the temperature; E can hardly depend appreciably on the pressure, except in cases where, by the application of external pressure, the number of collisions per second becomes great enough to influence the internal structure of the molecule, as, for example, when great pressure produces crystallizations and combinations. In the most general case, then, we have

to consider E as possibly a function of both temperature and pressure. But we can first see how the supposition that E is constant will work. The equation (1) then states that, given E the size of the molecules, their total energy, and their law of force, then e, the mean distance apart of the molecules free from external force, is determinable. The equation specifies the law of expansion of the simplest solid free of external stress. For example, imagine that we know only that solids expand very slightly with rising temperature, then $\frac{1}{e}\Sigma\Sigma r\phi(r)$ is probably nearly constant, and therefore α must be nearly proportional to the kinetic energy, or the expansion from absolute zero is nearly proportional to the absolute temperature, which is the definite experimental result. But before discussing this equation any further, we may as well make it more general by taking account of external stress and removing the condition of isotropy.

Imagine the properties of our molecules to be different in different directions, and in such a manner that all the circumstances can be specified with reference to three rectangular axes. Let the paths and velocities of the molecules be such that they produce the same collisional pressure in the direction of the x axis as if they were an isotropic system with mean kinetic energy $mu^2/2$ per molecule, and similarly kinetic energy $mv^2/2$ and $mw^2/2$ along the y and z axes, so that $(mu^2+mv^2+mw^2)/2=3\mathrm{D}$, where D is the mean kinetic energy per molecule of the actual system. Let the mean positions of the molecules correspond to a parallelepiped distribution with sides ξ, η, ζ to the parallelepiped, so that the mean distance apart of the molecules along the x axis is ξ, and so on. Let the external stress be specified by pressures P, Q, R parallel to the three axes, and let the mean components of the swing of each molecule in its domain be α, β, γ, then for equilibrium parallel to the x axis we have merely to add P to the molecular pressure in equation (1), and make the necessary slight alterations to get

$$\frac{mu^2}{3\eta\zeta\alpha}-\mathrm{P}-\frac{1}{6\xi\eta\zeta}\Sigma r\phi(r)=0, \quad . \quad . \quad . \quad . \quad (2)$$

with two similar equations.

If ΞHZ are the values of ξ, η, ζ when the molecules are in contact, we have three equations of the form $\xi-\Xi=\alpha$. Hence, given Ξ, H, Z, u^2, v^2, w^2, P, Q, R, and the law of force, the problem of finding ξ, η, ζ is determinate ; that is, the law of expansion in the three directions with increase of kinetic

energy under a given stress. But if the separate components u^2, v^2, w^2 are not given, but only D the mean kinetic energy, then, given P, Q, R, D, that is to say the stress and the temperature as well as Ξ, H, Z, there are four relations connecting the six quantities u^2, v^2, w^2, ξ, η, ζ. Two other relations would make the connexion between energy and size in different directions quite determinate; it is the business of experiment to ascertain these two relations.

If the body is homogeneous and isotropic when free from external stress, then the equations (2) are a little simplified by the relation $\Xi=\mathrm{H}=\mathrm{Z}=\mathrm{E}$, and we have

$$\frac{mu^2}{3\eta\zeta(\xi-\epsilon)}-\mathrm{P}-\frac{1}{6\xi\eta\zeta}\Sigma r\phi(r)=0, \quad . \quad . \quad . \quad (3)$$

with two similar equations.

If, further, the body is subjected to hydrostatic pressure p only, so that $\mathrm{P}=\mathrm{Q}=\mathrm{R}=p$, then the three equations of form (3) reduce to the one

$$\frac{2\mathrm{D}}{3e^2(e-\mathrm{E})}-p-\frac{1}{6e^3}\Sigma r\phi(r)=0. \quad . \quad . \quad . \quad (4)$$

Thus, if the size of the molecules is given, and also the law of force, then the relation of pressure, volume, and kinetic energy is determinate. Accordingly, we are able to calculate the bulk-modulus of the solid (the reciprocal of its compressibility).

Let ω denote volume, then the bulk-modulus is $\omega dp/d\omega$, denoted by

$$k=\omega dp/d\omega=\frac{2}{3}\omega\frac{d}{d\omega}\left\{\frac{\mathrm{D}}{e^2(e-\mathrm{E})}-\frac{1}{4e^3}\Sigma r\phi(r)\right\}.$$

But $\omega=ve^3$, where v is the number of molecules per unit volume, and so

$$k=\frac{2}{3}\cdot\frac{e}{3}\frac{d}{de}\left\{\frac{\mathrm{D}}{e^2(e-\mathrm{E})}-\frac{1}{4e^3}\Sigma r\phi(r)\right\}. \quad . \quad . \quad . \quad (5)$$

We can go no further without the law of molecular force, so I will now use the law of force, which I have formerly discussed in connexion with gases and liquids (Phil. Mag. 5th ser. xxiv. & xxvii.), namely, $\phi(r)=3\mathrm{A}m^2/r^4$. Then

$$\Sigma r\phi(r)=\int_a^{\mathrm{R}}\frac{4\pi r^2 dr\,3\mathrm{A}m\rho r}{r^4},$$

where a is a length of the order of e, and R is a length of the order of the linear dimensions of the body.

$$\Sigma r\phi(r) = 12\mathrm{A}m\pi\rho \log \mathrm{R}/a.$$

On account of the smallness of a, $\log \mathrm{R}/a$ is approximately the same for all ordinary bodies, and then $\Sigma r\phi(r)$ for a given body is always proportional to the density, and for different bodies its value depends on that of a parameter A, which has a definite value for each body. Apart from all specification of the law of molecular force, if the potential energy and the virial of a number of molecules are proportional to the density of their distribution, and can be represented by such forms as $\mathrm{B}\rho$, where B is constant for each substance, the same conclusions will hold as those I am about to draw from the law of the inverse fourth power. My previous arguments in favour of the inverse fourth power law amounted to this, that that is the only simple natural law, like the law of gravitation, that will make the potential energy of a number of molecules and their virial both closely proportional to the density of distribution, as experiment shows they must be.

With the above value of $\Sigma r\phi(r)$ and with $\rho = m/e^3$, we have

$$k = \frac{2}{3}\frac{e}{3}\frac{d}{de}\left\{\frac{\mathrm{D}}{e^2(e-\mathrm{E})} - \frac{3\mathrm{A}m^2\pi \log \mathrm{R}/a}{e^6}\right\}$$

$$= \frac{2}{3}\frac{e}{3}\left\{-\frac{2\mathrm{D}}{e^3(e-\mathrm{E})} - \frac{\mathrm{D}}{e^2(e-\mathrm{E})^2} + \frac{18\mathrm{A}m^2\pi \log \mathrm{R}/a}{e^7}\right\}.$$

But in the absence of external stress (4) becomes

$$\frac{\mathrm{D}}{e^2(e-\mathrm{E})} = \frac{3\mathrm{A}m^2\pi \log \mathrm{R}/a}{e^6},$$

and hence

$$k = \frac{2}{3}\frac{e}{3}\left\{\frac{4\mathrm{D}}{e^3(e-\mathrm{E})} - \frac{\mathrm{D}}{e^2(e-\mathrm{E})^2}\right\}. \quad . \quad . \quad (6)$$

2. *Testing of the Equations on the supposition that the Molecules are unalterable.*—Suppose that E is constant, then if b is the mean coefficient of linear expansion between zero and θ which corresponds to kinetic energy D, then $(e-\mathrm{E})/e = b\theta$, and if c is the mean specific heat between zero and θ, then $\mathrm{D} = \mathrm{J}mc\theta$, where J is the mechanical equivalent of heat, if we suppose that all the energy of the molecules exists in their vibrations as wholes; if not, then we must write $\mathrm{D} = h\mathrm{J}cm\theta$, where h is a fraction probably not differing much from unity. Thus we have

$$k = \frac{2}{3}h \cdot \frac{\mathrm{J}cm}{3bm/\rho}\left(4 - \frac{1}{b\theta}\right). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Even at the melting-point $1/b\theta$ for most metals is about 50, so that at ordinary temperatures 4 is small in comparison with $1/b\theta$. Neglecting 4 for the present, and remembering that c and b vary only to a small extent with temperature, and that cm, by Dulong and Petit's law, is the same for all metals, we can write, putting $h=1$,

$$k=-\frac{2}{9}\frac{\mathrm{J}cm}{b^2\theta m/\rho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

approximately, and assert that theoretically the bulk-modulus varies inversely as the temperature, and that the product $kb^2\theta m/\rho$ is the same for all metals. This result makes the bulk-modulus infinite at absolute zero, which, of course, is merely the result of our assumption that the change of volume of the molecules produced by collisions is negligible. At any rate the bulk-modulus at absolute zero is probably very large, that is, the molecules are probably only slightly compressible, as will be seen later on.

In our equations (7) and (8) for k we know all the quantities on the right-hand side (if $h=1$) for the metals, and we also have some quasi-experimental determinations of k, so that we can proceed to test how our assumption of E being constant will hold. The values of k are not purely experimental, because they are not obtained by direct measurement, but by calculations from other elastic measurements on the assumption that the metals are homogeneous isotropic solids. In such solids k is connected with the rigidity n, and Young's modulus q by the relation $k=nq/(9n-3q)$.

When k is calculated from the experimental values of n and q, the worth of the result depends entirely on the nearness to perfect isotropy of the solid. Thus, on the assumption of perfect isotropy, it is possible to calculate a value of k for many metals at 15° C. from the average values of n and q given above in Tables III. and VII. Tomlinson has given (Phil. Trans. 1883) values of k calculated from his measurements of n and q; and there is this advantage in using his values, that n and q were measured on the same specimen. Amagat has found (*Compt. Rend.* cviii.) values of k for a few bodies by measuring q, and also the change of volume produced by external pressure on hollow cylinders, and then calculating on the assumption of perfect isotropy. It will be shown afterwards that the metals are at least nearly isotropic, but yet we must assume that all our values of k for the metals are only more or less rough approximations to true values, because small departures from perfect isotropy produce large

errors in the value of k given by the formula for perfect isotropy.

The following Table contains in the row k_1 the values of k calculated from my average values of n and q given in Tables III. and VII., in k_2 Tomlinson's values, in k_3 Amagat's, and in k_4 the values found from equation (7) above, using Fizeau's values of b. The temperature is 15° C. in all. In the last row are given the values of the ratio of k_4 to the mean of k_1, k_2, and k_3.

	Cu.	Ag.	Au.	Mg.	Zn.	Al.	Sn.	Pb.	Fe.	Pt.
$10^{-6}k_1$...	2500	690	1370	325	900	810	imp.	86	2000	990
$10^{-6}k_2$...	980	930	...	...	350	320	130	76	1500	590
$10^{-6}k_3$...	1170	...	...	...	...	...	...	360	1470	
$10^{-8}k_4$...	970	520	980	190	250	325	264	134	2000	2800
Ratio ...	63	64	71	59	40	58	203	77	120	350

There are large discrepancies in the quasi-experimental values of k; for example, in the case of tin k_1 is impossible, because $9n-3q$ is negative; accordingly tin is so far from being reliably isotropic as to make attempts at calculating k illusory. If, besides tin, we reject platinum, we find fairly good agreement amongst the values of the ratio of k_4, the theoretical value, to the mean quasi-experimental value. The mean value of the ratio, leaving out iron, is 62, and including iron is 69; so that we can say that the theoretical values of the bulk-modulus of the metals, on the assumption that the molecules do not change in size with changing temperature, are about 70 times the actual values. Thus, while the assumption of constant size in molecules is proved by this comparison to be untenable, the general form of our equation receives some partial verification from it, as it shows $kb^2\theta m/\rho$ to be nearly the same for 8 out of 9 metals, and this is what the form of our equation demanded.

But fortunately there is a more satisfactory comparison to be made between theory and experiment in the matter of latent heats of melting. We cannot imagine our equation to bridge the gap in continuity between the solid and liquid states and calculate the latent heat by the formula

$$\lambda = \int_{v_1}^{v_2} \theta \partial p / \partial \theta \, dv,$$

where v_2 and v_1 are the volumes of unit mass in the liquid and solid states. But without any bridging of the gap in continuity we have the thermodynamic relation

$$\lambda = (v_2 - v_1)\theta dp/d\theta,$$

where $dp/d\theta$ means now the rate of increase of the melting-pressure with the melting-temperature. Now, according to our theory, melting occurs when molecules are able to escape from imprisonment by their neighbours, that is, when the space between molecules attains a certain value relatively to the size of the molecules. Hence, if the size of the molecules is invariable, melting must always occur for the same value of e whatever the pressure is, and we have $dp/d\theta$ of the last formula the same as $\partial p/\partial\theta$ taken from our equation with the condition $e=$constant.

$$\frac{\partial p}{\partial \theta} = \frac{2d\mathrm{D}\ d\theta}{3e^2(e-\mathrm{E})} \text{ and } \lambda = \frac{2\mathrm{D}(v_2-v_1)}{3e^2(e-\mathrm{E})} \quad . \quad . \quad . \quad . \quad (9)$$

But on this view of melting the latent heat may be calculated in another manner, for on this purely mechanical view it must be the energy supplied to produce the change of potential energy that accompanies the change of density on liquefaction. Hence $\lambda=\mathrm{B}(\rho_1-\rho_2)$, and neglecting p in our equation, this

$$= \frac{2\mathrm{D}}{3e^2(e-\mathrm{E})} \cdot \frac{\rho_1-\rho_2}{{\rho_1}^2};$$

$$\therefore\ \lambda = \frac{2\mathrm{D}(v_2-v_1)}{3e^2(e-\mathrm{E})} \cdot \frac{v_1}{v_2} = \frac{2\mathrm{D}(v_2-v_1)}{3e^2(e-\mathrm{E})} \text{ nearly,}$$

as before. Hence, remembering that $e^3=m/\rho$, $\mathrm{D}=\mathrm{J}cm\theta$, and $e-\mathrm{E}=eb\theta$ nearly, we can write

$$\lambda = \frac{2cm}{3bm} \cdot \frac{\rho_1-\rho_2}{\rho_1} \text{ calories.} \quad . \quad . \quad . \quad . \quad (10)$$

Person (*Ann. de Ch. et de Ph.* sér. 3, t. 24) has found the latent heats of several metals, and Vincentini and Omodei (Wied. *Beibl.* xii.) have found the change of volume at the instant of melting for lead, cadmium, tin, mercury, and other bodies; and Roberts and Wrightson (Nature, xxiv.), amongst other data, give the densities of melted zinc and silver, whose densities just before melting can be calculated approximately by means of their coefficients of expansion, though this is not so satisfactory as a direct measurement. The mean coefficient of expansion b of solid mercury is not known, but can be found by the relation $b\mathrm{T}m^{\frac{1}{3}}=\cdot044$, where T is melting-point, to be afterwards discussed. Person, in his calculations, intentionally ignored the increase of specific heat with temperature, but if we put $c=c_0(1+\alpha t)$ and use the values of α given by Naccari (Wied. *Beibl.* xii.) from experiments

between zero and 320° C., we can get the true latent heats we require by subtracting $\frac{1}{2}\sigma_0\alpha T^2$ from Person's values. Thus we can compare our theoretical values of λ with the experimental in the case of six metals. The following Table contains the values of ρ_1 and ρ_2, Person's value of the latent heat λ_1, the true latent heat λ_2, and the value λ_3 calculated on the supposition that the molecules are invariable :—

	Ag.	Zn.	Cd.	Hg.	Sn.	Pb.
ρ_1.....	9·92	6·85	8·366	14·19	7·183	11·00
ρ_2.....	9·51	6·48	7·99	13·69	6·99	10·64
λ_1.....	21·1	28·1	13·6	2·8	14·2	5·4
λ_2.....	16·2	24·5	12·5	2·8	12·8	4·8
λ_3.....	81·0	117·0	53·3	9·7	46·0	23·6
Ratio λ_3/λ_2.	5·0	4·8	4·3	3·2	3·6	4·9

In the case of silver it was not safe to extrapolate for specific heat up to the melting-point of 954° C. from experiments up to 320°, so I made a determination of its mean specific heat between 20° and 860° in comparison with that of gold, which is known ; the result was ·0663, which, over a range of 934°, gives 61·9 calories in place of Person's 57. In the case of tin I used Tomlinson's determination of the specific heat, as Naccari omitted it. The ratio λ_3/λ_2 comes out nearly constant, especially if we omit mercury as uncertain on account of the smallness of λ, and tin as uncertain on account of its tendency to crystallize ; the mean value of the ratio for the other four metals is 4·75. In each case the calculated value of λ is about 4·75 times the experimental, and here again, while the actual equation and the assumption of inalterability in the molecules are not verified, the form of the equation is confirmed in a striking manner if we remember that the latent heat ranges from 2·8 for mercury to 28 for zinc. In other words equation (10) asserts that

$$2\sigma(\rho_1-\rho_2)/3\rho_1\lambda$$

is constant on purely theoretical grounds, and the tabulated comparison shows it to be constant, only that the value of the constant is, on the average, 4·75 instead of 1 ; still it is promising confirmation for the kinetic theory that it should be constant at all.

We may state, then, that collections of unaltering molecules, having the coefficients of expansion of the different metals, would, on the kinetic theory, have bulk-moduluses

about 65 times as large as the actual, and latent heats about 4·75 times as large.

3. *Testing of Equations on the supposition that the Molecules alter somewhat with Change of Temperature.*—The next step is to ascertain what modification in the assumptions so far made would bring theory and experiment into accord. If we return to the approximate expressions

$$(6) \quad k = -2\mathrm{D}\ 9e(e-\mathrm{E})^2$$

and

$$(9) \quad \lambda = 2\mathrm{D}(r_2 - r_1)\ 3e^2(e-\mathrm{E}),$$

we see at once that if E, which represents the linear dimensions of the molecule, were to diminish with rising temperature, then theory and experiment could be brought to better accord. Now the shrinking of molecules with rising temperature is a result required by the kinetic theory of gases, for the variation of the viscosity of gases with temperature is such as can be accounted for satisfactorily only by shrinkage of molecules with rising temperature.

Holman (Phil. Mag. 5th ser. vol. xxi.) has made a thorough comparison of the results of all the best measurements of the effect of temperature on the viscosity of air, including his own, and his series of curves shows that up to 250° C. the viscosity of air at any temperature is best given in terms of that at zero C. by the exponential formula

$$\eta_t = \eta_0(1+0{\cdot}00367t)^{0{\cdot}76} \quad \text{or} \quad \eta_\theta = \eta_{273}(\theta/273)^{0{\cdot}76},$$

where θ is absolute temperature. Now, according to the kinetic theory of gases, assuming the molecules to be spheres of sectional area σ_θ^2, and ignoring molecular attraction, we have

$$\eta_\theta = \eta_{273}(\sigma_{273}/\sigma_\theta)^2(\theta/273)^{\frac{1}{2}},$$

and hence

$$(\sigma_{273}/\sigma_\theta)^2 = (\theta/273)^{0{\cdot}26};$$

that is to say, the molecules shrink with rising temperature. Now Barus (Amer. Journ. Sci. 3rd ser. vol. cxxxv.) has given weighty support to this idea of molecular shrinking by pushing the study of the viscosity of air and hydrogen up to 1200° C., and showing that up to that temperature the viscosity of both gases is well represented by

$$\eta_\theta = \eta_{273}(\theta\ 273)^{\frac{2}{3}},$$

according to which

$$(\sigma_{273}\ \sigma_\theta)^2 = (\theta\ 273)^{\frac{1}{3}}.$$

Now both these formulæ for σ are derived by combining a theoretical equation with empirical formulæ, and in the theoretical equation molecular attraction is supposed not to exist. But the effect of molecular attraction on viscosity will partly account for the apparent shrinkage of molecules, because slowly moving molecules coming near to one another without actually colliding are swung round their common centre of mass by the action of molecular force, and are affected as regards their subsequent paths, as if they had suffered a collision. At high velocities two molecules, which pass close to one another without actual collision, shoot past one another with only a slight mutual deflexion; thus the molecules behave as if they had larger volumes at lower temperatures. This effect of molecular force on the temperature-variation of viscosity is a difficult problem in the kinetic theory of gases, which remains yet to be worked out. Steps towards its solution have been taken by Maxwell (Phil. Trans. 1867) and by L. Natanson (*Kinetische Theorie unvollkommener Gase*), but no definite enough result has yet been reached to give a quantitative estimate of the importance of molecular force in viscosity of gases. Yet from a general point of view we may feel pretty sure that in the case of hydrogen the large apparent shrinkage of the molecules cannot be traced entirely to the effect of molecular force, and must be regarded as a true phenomenon. If we take our deduction from Barus's experiments,

$$\sigma_{273}/\sigma_\theta = (\theta/273)^{1\frac{1}{2}},$$

we notice that, although θ ranges from 273° to 1489°, yet $\theta^{1\frac{1}{2}}$ ranges only from 1·60 to 1·84; and thus, while the formula for σ, if supposed to hold down to absolute zero, would give the impossible result of σ being infinite at zero, this impossible result is merely the consequence of trying to extrapolate with an empirical formula over a range seven times as great as that covered by experiment.

Accordingly, we can get no definite assistance from the present state of the theory of viscosity of gases, but only a general assurance that molecules shrink with rising temperature. For the law of shrinkage of the molecules of solids I will take the expression $E = E_0/(1+b'\theta)$, which, up to the melting-point, may more conveniently be used in the form $E = E_0(1-b'\theta)$, so that $e - E = E_0(b+b')\theta$.

The steps in the differentiation for finding the bulk-modulus are not affected by the variability of E with temperature: as before, we have (6),

$$k=\frac{2e}{9}\left\{\frac{4\mathrm{D}}{e^3(e-\mathrm{E})}-\frac{\mathrm{D}}{e^2(e-\mathrm{E})^2}\right\}$$
$$=-\frac{2\mathrm{D}}{9\mathrm{E}_0{}^3}\left\{\frac{1}{(b+b')^2\theta^2}-\frac{4}{(b+b')\theta}\right\}$$
$$=\frac{-2\mathrm{J}cm}{9(b+b')^2\theta m\rho}\{1-4(b+b')\theta\}\quad\ldots\quad(11)$$

whence, using the mean of the quasi-experimental values of k given above as k_1, k_2, k_3, and the other known experimental terms, we can get the values of b' for the metals.

But our expression for the latent heat will be altered by the variability of E. We have to find at what rate the melting-pressure varies with the melting-temperature for a collection of molecules that shrink with rising temperature. Now melting has chiefly to do with the mobility of the individual molecules. Each molecule of a solid, if it is not close to the surface, moves as if it were free from the action of molecular force, because the attractions of the molecules all round it equilibrate one another. Let us conceive molecular force not to exist, that is conceive a perfect gas compressed till its molecules hem one another into fixed mean positions, this will be identical with our solid; except that molecular pressure is replaced by external pressure, the condition of the individual molecules is the same. Now melting occurs when the molecules escape from their domains, and suppose this happens for values e, E, p, and θ of the variables: it is desired to find how much the temperature is to be raised to reach the melting-point when p is increased to $p+dp$. It is obvious that e/E must remain constant, and the only other condition is that the collisional pressure increase must be equal to dp. Hence, if in our equation we ignore the molecular-force term and find $dp/d\theta$ on the supposition that e/E is constant, we can take it as $dp/d\theta$ in the thermodynamic relation $\lambda=\theta(v_2-v_1)dp/d\theta$,

$$\theta dp/d\theta=\frac{2\mathrm{D}}{3e^3(1-\mathrm{E}/e)}\left(1-\frac{3\theta}{e}\frac{de}{d\theta}\right).$$

But $e/\mathrm{E}=\mu$ say, and E is a function of θ only, so that $de/d\theta=\mu d\mathrm{E}/d\theta=-\mu\mathrm{E}_0b'$,

$$\therefore\ de/ed\theta=-b'\mathrm{E}_0\,\mathrm{E}=-b'(1+b'\theta).$$

Hence at the melting-point,

$$\lambda=\frac{(v_2-v_1)2\mathrm{D}}{3e^2(e-\mathrm{E})}\{1+3b'\mathrm{T}(1+b'\mathrm{T})\}$$
$$=\frac{2cm(v_2-v_1)}{3(b+b')m/\rho}\{1+3b'\mathrm{T}(1+b'\mathrm{T})\}\ \text{calories.}\quad(12)$$

If we now compare our expressions (11) and (12) for the bulk-modulus and latent heat with those which before gave results respectively 6·5 and 4·75 times too large, and neglect for a moment the small terms, we see that in a general way the theoretical bulk-modulus (11) and the experimental would agree if b' were put equal to $7b$ as $8^2=64$, and the theoretical latent heat (12) would agree with the experimental if $b'=3{\cdot}75b$. But if in (11) and (12) we take account of the small terms and solve for b', we find that on the average the relation $b'=6b$ will bring the theoretical values of both the bulk-modulus and latent heat into accord with the experimental. The best way of showing this will be to tabulate the values calculated from (11) and (12) by means of the relation $b'=6b$, and compare them with the experimental. For the bulk-modulus the mean of k_1, k_2, k_3 given before is taken as the experimental value.

10^{-6} times the Bulk-modulus.

	Cu.	Ag.	Au.	Mg.	Zn.	Al.	Pb.	Fe.	Pt.
Quasi-Exp....	1550	810	1370	325	625	565	174	1660	790
Theory	1710	920	1790	310	410	560	216	3740	5310
Ratio	1·1	1·1	1·3	·96	·66	1·0	1·2	2·2	6·7

On the whole the values of the ratio show that $b'=6b$ brings experiment and theory into good accord as regards bulk-modulus.

Latent Heat.

	Ag.	Zn.	Cd.	Hg.	Sn.	Pb.
Exp. ...	16·2	24·5	12·5	2·8	12·8	4·8
Theory...	17 2	23·7	10·4	1·9	8·0	4·6
Ratio ...	1·06	·97	·83	·67	·63	·95

If, for the reasons given before, we attach less weight to the values for mercury and tin, the value of the ratio for the other four metals is satisfactorily near to 1.

4. *Further evidence of the Alteration of Molecules with Change of Temperature.*—It is important now to see what further justification there is for the idea that molecules shrink with rising temperature. The small amount by which metals expand on being heated from absolute zero to their melting-points, namely about 2 per cent. of their linear dimensions, has made it difficult to form a mechanical conception of molecular behaviour during melting, because if the molecules are really at rest against one another at absolute zero it is hard

to see how an increase of only 2 per cent. in the distance apart of the molecules can give them the freedom and mobility of the liquid state. But if while heat is driving the molecules apart from one another it is also shrinking each, the difficulty disappears, for if the shrinkage is six times the expansion then at the melting-point the distance apart of the molecules is nearly 16 per cent. greater than the diameter of the molecule; that is to say, the complete swing of the vibration is 16 per cent., and when two molecules have swung to their greatest distance apart that distance will be 16 per cent. greater than the diameter of the molecule. This is sufficient to make melting quite comprehensible. Let us take a definite instance: suppose four molecules at absolute zero in contact so that their centres form a square of side E_0, and as the temperature rises, suppose each to oscillate along a diagonal, then the maximum distance apart of the opposite molecules becomes $1{\cdot}16\sqrt{2}$ times the diameter of the molecule, that is 1·63 times, so that a molecule vibrating at right angles to the plane of the square towards its centre, would, if it arrived at the right moment, find an open space whose narrowest part is ·63 times its own diameter. This shows how, in the various combinations possible in a large number of molecules, several can occur favourable to the escape of a single molecule in a neighbourhood, and a sufficient number of such escapes, even though a small number, would upset the stability of the whole system, which falls into the mobility of a liquid. This theory of melting can be roughly tested by experiment; it is only necessary to agitate a number of equal spheres in a closed box and observe what ratio the free space bears to the volumes of the spheres when each sphere acquires a noticeable amount of mobility. I took a box which, when closed, just held 100 marbles, with five specially coloured ones placed near the centre, and then noted how many had to be removed from the box to allow the five coloured ones to scatter on agitation; a slight motion of the five as a body was not accepted as a sign of mobility. It was necessary to remove 16 to get slow and partial scattering of the central 5, and 20 or 25 to get quick and decided scattering. Thus for mobility among a set of marbles the free volume must be between 25 and 33 per cent. of the volume of the marbles. Of course the circumstances are in most ways vastly different from those of perfectly rebounding swiftly moving molecules, but the comparison was worth making in passing. In the case of molecules mobility is reached when the free volume is $1{\cdot}16^3 - 1$, or 50 per cent. of the volume of the molecules. But the melting volumes of the metals give more definite evidence.

According to the kinetic theory of solids now under discussion, it is necessary, if the molecules of different metals are not much different in shape, that the ratio of the domain of the molecule at the melting-point to the volume of the molecule should be the same for all, because melting is merely the result of the domain reaching a size at which the molecule escapes from it. Hence $(1+b\mathrm{T})(1+b'\mathrm{T})$ is to be the same for all, that is $b\mathrm{T}+b'\mathrm{T}$ is to be constant; but $b'=6b$, hence $b\mathrm{T}$ is to be constant. Now in a previous paper (Phil. Mag. Oct. 1890) I mentioned that $b\mathrm{T}m^{\frac{1}{6}}$ is nearly constant for the metals, and used the result to calculate the periods of vibration of the molecules of solids at their melting-points with satisfactory results. But the range in the value of $m^{\frac{1}{6}}$ for the metals is not great, and it will be worth while tabulating side by side the values of $b\mathrm{T}$ and $b\mathrm{T}m^{\frac{1}{6}}$. Fizeau's values of b are used.

	Cu.	Ag.	Au.	Mg.	Zn.	Cd.	Al.
$1000\ b\mathrm{T}$.....	22	24	19	27	20	18	26
$1000\ b\mathrm{T}m^{\frac{1}{6}}$...	45	52	45	47	40	40	45

	In.	Tl.	Sn.	Pb.	Fe.	Co.	Ni.
$1000\ b\mathrm{T}$.....	19	17	11	18	25	26	24
$1000\ b\mathrm{T}m^{\frac{1}{6}}$...	41	41	25	43	49	51	47

	Ru.	Rh.	Pd.	Os.	Ir.	Pt.
$1000\ b\mathrm{T}$.....	20	19	21	18	16	18
$1000\ b\mathrm{T}m^{\frac{1}{6}}$...	43	42	45	44	37	44

This comparison shows that the requirement of theory that $b\mathrm{T}$ should be constant is approximately satisfied, $b\mathrm{T}$ having a mean value ·021 when tin is excluded; but as $b\mathrm{T}m^{\frac{1}{6}}$ is more nearly constant, having a mean value ·044, it is evident that the power of a molecule to break away from its domain depends slightly on its mass, that dependence being expressed in the empirical relation $b\mathrm{T}m^{\frac{1}{6}}=\text{constant}$.

5. *Periods of Vibration of the Molecules of Metals.*—As the vibrational motion of the molecules is fundamental to the kinetic theory of solids here unfolded, it will be well at this stage to secure such support for the theory as is given by the harmonic relations I have shown to exist among the periods of vibration of the molecules of metals at their melting-points (Phil. Mag. Oct. 1890). The full swing of a molecule in one direction is

$$e-\mathrm{E}=\mathrm{E}_0(b\mathrm{T}+b'\mathrm{T})=7\mathrm{E}_0b\mathrm{T}.$$

Let M stand for the molecular weight of a molecule referred in the ordinary way to that of hydrogen, and let H denote the real mass of a molecule of hydrogen, then the swing of a molecule is.

$$7(\mathrm{MH}/\rho)^{\frac{1}{3}}\cdot 044/\mathrm{M}^{\frac{1}{6}}.$$

But its translatory kinetic energy is

$$\tfrac{1}{2}\mathrm{MH}v^2 = Jc\mathrm{MHT},$$

$$\therefore \qquad v = \sqrt{2Jc\mathrm{MT}/\mathrm{M}},$$

and accordingly the period of a complete vibration is

$$p = \frac{\mathrm{M}^{\frac{2}{3}}}{\rho^{\frac{1}{3}}\mathrm{T}^{\frac{1}{2}}}\cdot\frac{2\times 7\times\cdot 044\mathrm{H}^{\frac{1}{3}}}{\sqrt{2Jc\mathrm{M}}}.$$

For comparative values we can drop the whole numerical factor and take $\mathrm{M}^{\frac{2}{3}}/\rho^{\frac{1}{3}}\mathrm{T}^{\frac{1}{2}}$ as measuring the relative periods. In the subjoined table I replace the erroneously copied values for the beryllium family, given in my former paper, by the correct ones.

Relative Periods, $\mathrm{M}^{\frac{2}{3}}/\rho^{\frac{1}{3}}\mathrm{T}^{\frac{1}{2}}$.

Li.	Na.	K.	Rb.	Cs.	Cu.	Ag.	Au.
·205	·43	·66	·96	1·22	·21	·29	·35
Be.	Mg.	Ca.	Sr.	Ba.	Zn.	Cd.	Hg.
·107	·22	·34	·51	·63	·32	·47	·94
Al.	La.	Ga.	In.	Tl.			
·20	·55	·54	·57	·65			
Fe.	Co.	Ni.	Ru.	Rh.	Pd.	Os.	Ir.	Pt.
·16	·16	·17	·21	·20	·24	·23	·25	·27

In the Li family the periods run as 1, 2, 3, 4·5, 6 with the copper sub-family connected; in the Be family the periods run as 1, 2, 3, 4·5, 6, with the zinc sub-family related in somewhat the same way as the copper to the lithium, but not exactly. Al and La have periods nearly as 2 to 6. The other periods do not call for comment at present; but it is worth noting that the periods of the Be family are half those of the Li family. These beautiful harmonic relations almost amount to a proof that the expansion of the metals is a true measure of the amplitude of vibration of their molecules. It will be interesting to try to get an absolute value of one of these periods, and compare it with known periods of light- and heat-vibrations. Sir W. Thomson estimates that

there are between 3×10^{24} and 10^{26} molecules in a cubic centimetre of ordinary liquids and solids. Now the limiting volume of a gramme of hydrogen is about 4 cubic centimetres, so that if we take 10^{25} as the number of molecules in a cubic centimetre of hydrogen $\mathrm{H}=2{\cdot}5\times10^{-26}$ gramme, and the numerical factor dropped above becomes 8×10^{-14}, which makes the absolute period of the Lithium molecule $1{\cdot}6\times10^{-14}$ second; that is to say, there are 6×10^{13} complete vibrations of the molecule in a second. Now the A line of the spectrum represents $3{\cdot}945\times10^{14}$ vibrations, and the H_2 line $7{\cdot}628\times10^{14}$ vibrations per second, while in the dark part of the spectrum Langley has found a line of $1{\cdot}1\times10^{14}$, and in the radiation of bodies below 100° C. a line of 2×10^{13} vibrations in a second. Accordingly, the periods of vibration of the molecules of the metals at their melting-points fall within the limits of actually measured periods of non-luminous vibrations. This fact supplies good general verification to the theory, and shows how interesting a bolometric study of the radiation of solids just about to melt would be.

6. *Comparison of the Theoretical Variation of* Young's *Modulus with Temperature with the Experimental.*—The next subject to apply the theory to with advantage is the theoretical law of variation of Young's modulus with temperature for comparison with the experimental results given in the introduction. The metals, as will yet be shown, may be assumed to be approximately isotropic. In isotropic solids the relation between q, n, and k is $q=9kn/(3k+n)$. Now in the introduction it was shown for all the metals that $n/\mathrm{N}=1-(\theta/\mathrm{T})^2$, where N is rigidity at absolute zero, and from the theoretic equation (11) we have the values of k at all temperatures, and

$$q=\frac{3\mathrm{N}\{1-(\theta/\mathrm{T})^2\}}{1+\mathrm{N}\{1-(\theta/\mathrm{T})^2\}/3k}.$$

Now, according to (11), k is infinite at absolute zero, which we will interpret to mean that it is very large, and hence Q the value of Young's modulus q at absolute zero is 3N. Accordingly we have

$$\mathrm{Q}\{1-(\theta/\mathrm{T})^2\}(1/q-1/9k)=1 \quad . \quad . \quad . \quad (13)$$

as the definitely prescribed law of variation of Young's modulus with temperature. Because of this definite theoretic relation I did not, in the introduction, dwell on the demonstration of any empiric relation, but the values given for different temperatures and different metals will now furnish a

good test of the kinetic theory of solids. The best way to apply the test will be to calculate for each metal from the observed values of η and the theoretic values of k the values of Q,—these should come the same. For example, according to my experiments on zinc the values of $\eta 10^{-6}$ at absolute temperatures 289°, 333°, and 376° are 821, 758, and 682, and the corresponding values of $Q10^{-6}$ are 1280, 1320, and 1320, which satisfy well the requirement of constancy. Kiewiet's values for zinc, found by the method of bending at 283°, 325°, and 353°, are 1031, 975, and 924, which give for $Q10^{-6}$ the values 1710, 1800, and 1870, which do not satisfy the condition of constancy. It will be seen from equation (13) that a good deal depends on a correct absolute value of η, as well as on the relative values at different temperatures. For the other metals I will simply give the values of $Q10^{-6}$ calculated from 3 values of η at temperatures from 289° to 376° on the absolute scale. For tin 880, 890, and 990, and according to Kiewiet 740, 750, and 720; lead 326, 332, and 339; magnesium 439, 443, and 433; copper 1590 and 1540; aluminium 818 and 839; aluminium unannealed 735, 746, and 752; and iron 2253, 2241, and 2226. It is evident that experimental uncertainties do not at present let us expect any better agreement between theory and experiment than that just shown. But there is another form in which the same comparison can be made. One of the results of equation (13) is that Young's modulus at absolute zero is 3 times the rigidity. Now by means of (13) we can from the mean values of η at 15° C. given in Table VII. calculate the values of Q, and compare them with the values of N, given in Table V.

TABLE VIII.

10^{-6}Q or 10^{-6} times Young's modulus at absolute Zero.

	Cu.	Ag.	Au.	Mg.	Zn.	Cd.	Al.
Q.....	1390	860	840	490	1490	1040	840
Q/N...	3·1	2·9	2·9	3·0	3·5		3·2

	Sn.	Pb.	Fe.	Ni.	Co.	Pd.	Pt.
Q.....	700	270	2170	2460	1970	1130	1690
Q/N...	3·5	2·3	2·8	3·2			2·6

With the exception of platinum, the only metals for which the departure of N/Q from the value 3 is beyond the limits of experimental error are zinc, tin, and lead, the metals for which the results of different experimenters disagree most, as

shown in the compilation of data given in the introduction. These disagreements would seem to indicate that even if these metals can be got in an approximately isotropic state at all, their isotropy is easily disturbed, but this point will be returned to immediately. The mean value for the ratio Q/N for the 7 metals Cu, Ag, Au, Mg, Al, Fe, and Ni is 3·0, and accordingly it appears that these metals may be regarded as isotropic, and as having molecules so nearly incompressible as to give the relation Q=3N characteristic of incompressible molecules.

The study of the ratio Q/N leads naturally to the famous controversy amongst elasticians as to whether there is a fixed value of the ratio of lateral contraction to longitudinal extension for all isotropic bodies subject to traction; but this matter had better be postponed a little until we have seen what account the kinetic theory can give of rigidity. This is the most important point in a theory of solids, and as I have already pointed out that no static theory can give an adequate explanation of rigidity, there is great interest in seeing how the kinetic theory will fare.

7. *Rigidity according to the Kinetic Theory.*—The fundamental equation for a solid, homogeneous and isotropic and free from external force is

$$(4) \qquad \frac{2D}{3e^2(e-\bar{E})} - \frac{1}{6e^3}\Sigma r\phi(r) = 0,$$

or

$$\frac{2D}{3e^2(e-\bar{E})} - B\rho^2 = 0.$$

Suppose the solid now subjected to a pure shearing stress specified by a traction P parallel to the axis of x, and a pressure P parallel to that of y: the traction counts as a pressure $-P$, and the corresponding strains are an elongation of e to ξ parallel to x, and a contraction of e to η parallel to y. The strained body is no longer isotropic, and equations (3) are applicable to it if we write $-P$ for P, and put Q=P and R=0. Let $\xi = e + \delta\xi$, and $\eta = e + \delta\eta$, and $\zeta = e$, then $\delta\eta = -\delta\xi$. The effective kinetic energies in different directions are no longer equal each to D, but become $\frac{1}{2}mu^2$, $\frac{1}{2}mv^2$, and $\frac{1}{2}mw^2$, which will be denoted by D_1, D_2, and D_3, and let $D_1 = D + \delta D_1$ and so on. We do not know at present how we are to express the condition that the shear is made at constant temperature, for when the effective kinetic energy is different in different directions, what is the relation between these different energies and temperature? All that we can assert is $\delta D_2 = -\delta D_1$. Now the shear produces a change of volume

only of the second order, so that $\Sigma r\phi(r)/6e^3$ may be regarded as unaltered, and after the shear we have

$$\tfrac{2}{3}\cdot\frac{\mathrm{D}+\delta\mathrm{D}_1}{(e+\delta\eta)e(e+\delta\xi-\mathrm{E})}+\mathrm{P}-\frac{1}{6e^3}\Sigma r\phi(r)=0.$$

Replace the last term by its value $2\mathrm{D}/3e^2(e-\mathrm{E})$, and expand the first term, then

$$-\mathrm{P}=\tfrac{2}{3}\frac{\mathrm{D}}{e^2(e-\mathrm{E})}\left(\frac{\delta\mathrm{D}_1}{\mathrm{D}}-\frac{\delta\eta}{e}-\frac{\delta\xi}{e-\mathrm{E}}\right),$$
$$=\tfrac{2}{3}\frac{\mathrm{D}}{e^2(e-\mathrm{E})}\left(\frac{\delta\mathrm{D}_1}{\mathrm{D}}+\frac{\delta\xi}{e}-\frac{\delta\xi}{e-\mathrm{E}}\right).$$

P is the shearing stress, and $2\delta\xi/e$ is the shear, so that the rigidity n is $\mathrm{P}e/2\delta\xi$,

$$n=-\tfrac{1}{3}\frac{\mathrm{D}}{e^2(e-\mathrm{E})}\left(\frac{\delta\mathrm{D}_1}{\delta\xi}\frac{e}{\mathrm{D}}-\frac{e}{e-\mathrm{E}}+1\right)\quad.\quad(14)$$

This equation gives a statement of what rigidity is according to the kinetic theory; it depends on the rate of change of the effective kinetic energy in a direction with the change of the distance apart of the molecules in that direction. This ratio of $\delta\mathrm{D}_1$ to $\delta\xi$ is fundamental in the theory of solids; the condition for zero rigidity or fluidity is

$$e\delta\mathrm{D}_1/\mathrm{D}\delta\xi=e/(e-\mathrm{E})-1.$$

It would be possible to calculate the ratio of $\delta\mathrm{D}_1$ to $\delta\xi$ on purely theoretical ground with the aid of suppositions as to the distribution of kinetic energy in different directions and its relation to temperature, but this is not worth doing at present; it will only be shown shortly that even in solids $\delta\mathrm{D}_1/\delta\xi$ differs only from the large number $e/(e-\mathrm{E})$ by a small number, that is, a number not much greater than 1. But first it may be as well to determine Young's modulus from our equations in the same way as we have just found the rigidity. It is only necessary to put $-\mathrm{P}$ for P_1, $\mathrm{Q}=0$, $\mathrm{Z}=0$, $\zeta=e+\delta\zeta$, $\delta\zeta=\delta\eta=-\sigma\delta\xi$, and replace $\Sigma r\phi(r)/6e^3$ by $\mathrm{B}m^2/\xi^2\eta^2\zeta^2$, and to expand, to get the following equations in which the variables are accented to distinguish the conditions of variation from the former ones:

$$\left.\begin{aligned}
-\mathrm{P}&=\tfrac{2}{3}\frac{\mathrm{D}}{e^2(e-\mathrm{E})}\left(\frac{\delta\mathrm{D}_1'}{\mathrm{D}}+\frac{\delta\eta'+\delta\zeta'+2\delta\xi'}{e}-\frac{\delta\xi'}{e-\mathrm{E}}\right),\\
q&=\frac{\mathrm{P}e}{\delta\xi'}=-\tfrac{2}{3}\frac{\mathrm{D}}{e^2(e-\mathrm{E})}\left(\frac{\delta\mathrm{D}_1'}{\delta\xi'}\frac{e}{\mathrm{D}}-2\sigma+2-\frac{e}{e-\mathrm{E}}\right),\\
\frac{\delta\mathrm{D}_2'}{\mathrm{D}}&=\frac{\delta\mathrm{D}_3'}{\mathrm{D}}=\left(3\sigma-1-\frac{\sigma e}{e-\mathrm{E}}\right)\frac{\delta\xi'}{e}.
\end{aligned}\right\}\quad(15)$$

Now at absolute zero our collection of molecules is supposed to be practically incompressible, so that $Q=3N$, and $\sigma=\frac{1}{2}$; hence for N we have the two values, the limit of

$$\frac{1}{3}\frac{D}{e^2(e-E)}\left(\frac{\delta D_1}{\delta\xi}\frac{e}{D}-\frac{e}{e-E}+1\right),$$

and the limit of

$$\frac{2}{9}\frac{D}{e^2(e-E)}\left(\frac{\delta D_1'}{\delta\xi'}\frac{e}{D}-\frac{e}{e-E}+1\right).$$

These two forms and the value of $\delta D_2'$ above, which at absolute zero is given by $2e\delta D_2'/D\delta\xi'=1-e/(e-E)$, suggest that both $e\delta D_1/\delta\xi D$ and $e\delta D_1'/\delta\xi' D$ are nearly equal to $e/(e-E)$. If in the case of Young's modulus the condition for constant temperature were that the mean of the effective kinetic energies in all directions is constant or

$$\delta(D_1'+D_2'+D_3')=0,$$

then, from the values of $\delta D_2'$ and $\delta D_3'$ we get

$$\frac{e\delta D_1'}{\delta\xi' D}=\left(\frac{2\sigma e}{e-E}+2-6\sigma\right),$$

which at absolute zero would make q vanish, and therefore cannot be quite correct, but proves at all events that at absolute zero $e\delta D_1'/D\delta\xi'$ is nearly equal to $e/(e-E)$. The two expressions for N show that at absolute zero we may put

$$\frac{e\delta D_1'}{D\delta\xi'}=\frac{e}{e-E}+A,$$

where A is a constant the same for all bodies, and

$$\frac{e\delta D_1}{D\delta\xi}=\frac{e}{e-E}+B,$$

where B is the same for all bodies, and

$$B+1=\tfrac{2}{3}(A+1),$$

A and B are both numbers not large compared to 1. Then N is the limiting value of

$$\frac{1}{3}\frac{D(B+1)}{e^2(e-E)},$$

which, with $D=Jcm\theta$ and $e-E=7l\theta E_0$, gives

$$N=\frac{Jcm(B+1)}{21lm/\rho}; \quad . \quad . \quad . \quad . \quad . \quad (16)$$

cm is constant, so that we have this result, that the product Nbm/ρ is the same for all metals, and so also the product Qbm/ρ. The best manner of testing this last theoretical conclusion will be to tabulate the values of $7Qbm/Jcm\rho$ and $21Nbm/Jcm\rho$, and see whether all the metals give the same value for B + 1.

	Cu.	Ag.	Au.	Mg.	Zn.	Cd.	Al.
$7Qbm/Jcm\rho$ or B + 1...	4·6	4·6	3·2	5·0	10·5	10·9	5·9
$21Nbm/Jcm\rho$ or B + 1...	4·5	4·7	3·2	5·0	9·0		5·5

	Sn.	Pb.	Fe.	Ni.	Co.	Pd.	Pt.
$7Qbm/Jcm\rho$ or B + 1...	6·2	3·7	4·8	5·4	4·4	3·2	3·6
$21Nbm/Jcm\rho$ or B + 1	5·4	4·7	5·1	5·2			4·3

The values for zinc and cadmium are about double those for the other elements; if for the moment we take half of them as the true values, and take the mean of all, we get for B + 1 the value 4·6, the serious departures from which are in the case of gold 3·2, aluminium mean 5·7, tin mean 5·8, and palladium 3·2; in the case of palladium the fault lies probably in the absolute value of q at 15° C., which is the mean of Wertheim's static and kinetic values 980×10^6 and 1130×10^6, while before annealing they are 1180×10^6 and 1240×10^6. In the case of tin uncertain isotropy and experimental uncertainty explain the discrepance, but for gold and aluminium no adequate explanation is available except one suggested below. On the whole the theoretical conclusion is well borne out. In the case of zinc and cadmium, the fact that the product is double the normal value is connected with the fact that the molecules of zinc and cadmium are known in the vaporous state to be monatomic. The product $7Qbm/Jcm\rho$ is independent of m the molecular mass; but as we do not know the dynamical significance of the constant B + 1, we cannot tell whether or not it ought to be twice as large for monatomic molecules as for diatomic. The assertion that B + 1 must be the same for all metals goes on the assumption that they are dynamically similar systems of molecules at absolute zero; if they are not so, then the assertion no longer holds, and this may be the cause of the difference in the case of gold and aluminium.

The theoretical relation that Qbm/ρ is to be the same for all metals corresponds to Wertheim's empirical discovery that, if q is Young's modulus at 15° C., $q(m/\rho)^{\frac{1}{3}}$ is approximately the same for all the metals (*Ann. de Ch. et de Ph.* sér 3. t. xii.).

Tomlinson (Phil. Trans. 1883) has investigated the same relation. We have seen, in the experimental introduction, that the elastic properties of the metals correspond only at temperatures which are the same fraction of the melting-temperatures, and accordingly any relation connecting Young's modulus at a fixed temperature with molecular volume or domain must be empirical. Now as the coefficient of expansion b is roughly proportional to the molecular domain m/ρ, the relation $Qbm/\rho = \text{constant}$ becomes $Q(m/\rho)^2 = \text{constant}$ approximately, whence we see the origin of Wertheim's relation. There are various other approximate empirical relations discovered by different physicists which correspond to combinations of those already established on theoretical grounds in this paper, but there is no use in discussing them further.

8. *Ratio of Lateral Contraction to Elongation in* Young's *Experiment.*—We can now take up the famous question as to whether the ratio of lateral contraction to longitudinal extension in the Young's modulus experiment has the same value for all isotropic bodies, as asserted by various builders of statical molecular theories of elasticity, and as denied by the upholders of a science of elasticity apart from molecular considerations. As no statical theory founded on central forces can give a true account of rigidity, it seems useless to discuss a deduction of such theories, but the important point of getting a test for isotropy is involved. We see at once, from the results of the experimental introduction, that temperature is an important condition which has never been taken into account by the upholders of a constant ratio. In isotropic solids we have the following equations for σ the ratio of contraction to elongation :—

$$\sigma = (3k-2n)/2(3k+n) \quad \text{and} \quad \sigma = q/2n - 1.$$

Now we have seen experimentally that

$$n = \mathrm{N}\{1-(\theta/\mathrm{T})^2\},$$

and by theory (11)

$$k = -\tfrac{2}{9}\frac{\mathrm{J}cm(1-28b\theta)}{49b^2\theta m/\rho},$$

so that σ is a not simple function of the temperature. At absolute zero k is according to our theory very large, and may be regarded as infinite, while n remains finite, and therefore the value of σ at absolute zero is $\frac{1}{2}$. But again at the melting-point n is zero, while k is finite, so that at the melting-point σ again attains the value $\frac{1}{2}$. Now σ has been

measured directly for a few metals by Mallock (Proc. Roy. Soc. xxix.) by one method, and by Amagat (*Compt. Rend.* cviii.) by a quite distinct method, and also by an indirect method. We will compare the values given by the first equation for σ at 15° C. with these experimental values.

Values of σ at 15° C.

	Cu.	Zn.	Pb.
Theory	·38	·17	·33
Mallock	·35	·18	·37
Amagat	·32	...	·43

For iron theory gives a value ·41, while Mallock found for steel the value ·25, and Amagat for steel ·27, but Okatow (Pogg. *Ann.* cxix.) has shown that steel according to its treatment gives values of σ ranging from ·275 to ·40. If we calculate σ according to the second equation above, using the mean experimental values of q and n at 15°, as given in Tables III. and VII. of the introduction, we get the following values:—Cu ·42, Zn ·33, Pb ·13, Fe ·33. These values for zinc and lead are in complete disaccord with the experimental values, that for zinc being much too large, and that for lead much too small. Now in studying the values of the ratio Q/N, which ought theoretically to be 3, we found for zinc 3·5, and for lead 2·3; but as the values of Q and N are both calculated from the mean values of q and n at 15° C., it is very likely that there is experimental error in q and n as individual experimenters differ greatly in their values. Hence if 3 is the true value for Q/N for all the metals, q/n is wrong in the same proportion as Q/N; and if we multiply our values of q/n by 3, and divide by Q/N, and use the result in our second equation for σ, we shall see whether theory will thus eliminate the discrepancy above for zinc and lead as due to experimental uncertainty in q/n. Doing this, we get for Cu ·38, Zn 14, ·Pb ·47, and Fe 42, which agree well with the values given by the first equation for σ, and with the directly observed values of Mallock and Amagat.

This agreement of theory and experiment shows that all idea of a constant value for σ in the case of isotropic bodies must be abandoned, and, what is much more important, that the metals are at least approximately isotropic. Amagat has already shown by some fine experimental work (*Compt. Rend.* cviii.) that some metals and alloys are isotropic, although his method of calculation makes the proof a little more perfect than it actually is. His method is to measure Young's modulus directly by statical experiments; let P be the pressure

applied longitudinally to a cylinder of length L producing a change of length dL, then

$$q = \mathrm{PL}/d\mathrm{L} \quad (a).$$

He also observed directly the change of volume of the cylinder in this experiment, but

$$d\mathrm{V} = (1-2\sigma)\mathrm{VP}/q \quad (b);$$

hence these two experiments give a direct determination of σ. Again, he compressed the hollow cylinder of radii R and R_0 externally with hydrostatic pressure, and according to elastic theory, if the material of the cylinder is isotropic the change of volume is given by

$$d\mathrm{V} = (5-4\sigma)\mathrm{R}^2\mathrm{PV}/(\mathrm{R}^2-\mathrm{R}_0{}^2)q \quad (c).$$

Amagat used this equation and (b) to calculate σ and q from his data; but a somewhat more trustworthy method would be to substitute the directly observed value of q in (c) and so obtain σ for comparison with the direct value given by (a) and (b). To complete the available evidence for the isotropy of the metals and alloys I will reproduce Amagat's directly found values of σ and σ_1, his values got from (b) and (c) as σ_2, and values which I have calculated from (a) and (c) as σ_3.

	Steel.	Copper.	Brass.	Delta.	Lead.
σ_1	·268	·325	·324	·347	·431
σ_2	·269	·329	·330	·333	·425
σ_3	·263	·303	·301	·388	·493

The agreement is sufficient to justify the assumption of isotropy on which equation (c) is founded.

9. Dulong *and* Petit's *Law*, Joule *and* Kopp's *Law, and the Equation for Compound Solids*.—The physical meaning of Dulong and Petit's law of the constancy of the atomic heats of the elements has been a subject of speculation with chemists and physicists ever since its discovery. As the kinetic theory of gases in regarding temperature as proportional to kinetic energy of the molecule, required that apart from internal motion and work the molecular heats of all gases should be the same, it has been felt that a similar connexion between temperature and molecular kinetic energy is at the foundation of Dulong and Petit's law. The kinetic theory of solids makes this quite plain, that Dulong and Petit's law is simply the expression of the fact that temperature is proportional to the kinetic energy of the molecule, or, to be more accurate, of the atom. The meaning of Dulong and Petit's law becomes

still clearer when taken in conjunction with that of Joule and Kopp, that the molecular heat of a solid compound is the sum of the atomic heats of the component atoms. This means that the freedom of the atom within the molecule is such that each atom vibrates independently of the others. On this basis it is easy to sketch the investigation of the equations for a solid compound. Let us consider a compound whose molecule consists of n_1 atoms of an element A_1, n_2 of A_2, and so on. Suppose a cubical arrangement of molecules at distance e apart, then the number of molecules per unit area is $1/e^2$, and hence the number of atoms A_1 per unit area is $n_1^{\frac{2}{3}}/e^2$. Let m_1, m_2, and so on be the masses of the atoms, and v_1, v_2 their mean velocities, then the collisional pressure per unit area due to the atoms A_1 is $n_1^{\frac{2}{3}}m_1v_1^2/e^2\alpha_1 3$, if α_1 is the full swing of the atom in its domain. For the total collisional pressure we have the sum of such pressures for the different sorts of atoms. For the pressure due to molecular attraction it does not matter whether we consider the attractions of the atoms separately or of the entire molecules; if we take the entire molecules, then we get the former expression $\Sigma r\phi(r)/6e^3$. For a solid compound submitted to hydrostatic pressure p we have the equation

$$\frac{1}{3e^2}\left(\frac{n_1^{\frac{2}{3}}m_1v_1^2}{\alpha_1}+\frac{n_2^{\frac{2}{3}}m_2v_2^2}{\alpha_2}+\ \ldots\right)-p-\frac{1}{6e^3}\Sigma r\phi(r)=0.$$

Kinetically, then, a compound in the solid state behaves like a mechanical mixture of its component atoms, because the molecules are almost as close to one another as the atoms in the molecule. It is evident that a complete kinetic theory of compounds must be a very complicated affair.

10. *The Parameter of Molecular Force.*—Hitherto we have managed to dispense with a close knowledge of the molecular attraction because we have always managed to eliminate it by using the fact that when the external pressure is small we can put

$$\Sigma r\phi(r)/6e^3=2D/3e^2(e-E),$$

which is the fundamental equation for a solid free from external force. But it is desirable to obtain an independent estimate of molecular force for comparison with that given by this equation, and Quincke's measurements of the capillary tensions of the metals at their melting-points give an excellent opportunity (Pogg. *Ann.* cxxxv. and cxxxviii.).

I have shown (Phil. Mag. 5th ser. vol. xxvii.) that if the law of molecular force is $3Am^2/r^4$ then the surface-tension is proportional to $Am^{\frac{1}{2}}\rho^{\frac{5}{3}}$. Let us denote the surface-tension by

s, then A the parameter of molecular force is proportional to $s/m^{\frac{1}{3}}\rho^{\frac{5}{3}}$. But if $\phi(r) = 3\mathrm{A}m^2/r^4$, then

$$\Sigma r\phi(r) = 12\mathrm{A}mn\pi\rho \log \mathrm{R}/a,$$

where $\log \mathrm{R}/a$ is nearly the same for all bodies not excessively small or large; hence

$$\Sigma r\phi(r)/6e^3 = 2\mathrm{A}\rho^2\pi \log \mathrm{R}/a = 2\mathrm{D}/3e^2(e-\mathrm{E}) = 2\mathrm{J}cm\rho/21mb,$$

or A is proportional to $cm/mb\rho$, or, as cm is constant, to $1/mb\rho$. Thus $s/m^{\frac{1}{3}}\rho^{\frac{5}{3}}$ is proportional to $1/mb$, or $bsm^{\frac{2}{3}}/\rho^{\frac{2}{3}}$ is constant It is to be noticed that while $\Sigma r\phi(r)/6e^3$ or $2\mathrm{J}cm\rho/21mb$ is independent of the molecular mass, the surface-tension $r\mathrm{A}m^{\frac{1}{3}}\rho^{\frac{5}{3}}$ is not, so that if the molecular weights of the metals are not all the same multiple of the atomic weights, exceptional metals will give exceptional values of $bsm^{\frac{2}{3}}/\rho^{\frac{2}{3}}$.

The following is a list of the values of $1000\,bsm^{\frac{2}{3}}/\rho^{\frac{2}{3}}$, s being given in milligrammes per millimetre. Where Quincke found two values of s by different methods, both are given. In the case of lead the surface-tension was determined by myself.

	Pt.	Pd.	Au.	Au.	Ag.	Ag.	Sn.	Pb.
s	169	136	100	131	43	80	60	34
$1000\,bsm^{\frac{2}{3}}/\rho^{\frac{2}{3}}$	7·3	7·4	7·4	9·7	4·0	7·5	8·7	6·9

	Zn.	Zn.	Cd.	Na.	K.	Hg.	Fe.	Fe.
s	88	83	71	26	37	59	102	97
$1000\,bsm^{\frac{2}{3}}/\rho^{\frac{2}{3}}$	11·4	10·8	13·6	14·4	26	28	4·7	4·4

The value of the surface-tension of iron is uncertain, as is the case also with sodium and potassium ; for the value of b for Hg, Na, and K, I used the relation $b\mathrm{T}m^{\frac{1}{3}} = \cdot 044$. The mean value of $1000bsm^{\frac{2}{3}}/\rho^{\frac{2}{3}}$ for Pt, Pd, Au, Ag, Sn, and Pb is 7·4, for Zn and Cd it is 12·3, which is once and a half as large or about $2^{\frac{2}{3}}$ as large, for Na it is twice as large, and for Hg and K four times. These relations and the whole subject of surface-tension in melted solids require further investigation. I have touched on the matter here to show that in the kinetic theory unfolded, the law of molecular force has not been lost sight of.

There are many phenomena of solids that invite investigation by the light of a kinetic theory, but it has seemed better to me to confine the present paper to the broad fundamental ones. One of the results of the inquiry is that the molecules of solids so nearly fill up their domains that the phenomena

of crystalline form are the outward results of the form of the molecule ; this has often been imagined to be the case, but the kinetic theory proves it. It is hardly necessary to enumerate the paths of experimental and theoretical investigation opened by a kinetic theory of solids ; but it is obvious that a kinetic theory of liquids requires to be seen to.

Melbourne, April 1891.

LXIV. *Note supplementary to a Paper on the Solitary Wave.* By J. McCowan, *M.A., B.Sc.**

IN the concluding section of a paper "On the Solitary Wave," printed in the July number of the Philosophical Magazine, I offered a brief criticism of certain views of Sir George Stokes, which are contained in a paper 'On the Theory of Oscillatory Waves,' republished in the first volume of his Collected Papers, on the possibility of a solitary wave being propagated without change of form. He has, however, privately called my attention to the fact that not only had he himself seen the error of his former opinion, but had, in a paper "On the Highest Wave of Uniform Propagation" (Proc. Camb. Phil. Soc. vol. iv.), suggested a method by which the solitary wave might be approximated to by a sort of trial and error process, though he had not attempted the approximation itself, which would be laborious. He has also published a note to this effect in the September number of the Philosophical Magazine, which, however, I have only just seen, owing to my absence from town during the summer recess. I greatly regret that, in ignorance of his more recent paper, I should have offered any criticism of Prof. Stokes's earlier views, a criticism to which I was only led by the consideration that it would be impossible to pass over in silence the opinions of an authority of such eminence when they were in conflict with the results of my paper.

In his last "Note on the Theory of the Solitary Wave," already referred to, Prof. Stokes has explained how he had previously been led to a wrong conclusion, and this need not, I think, call for any remark on my part; but he has further offered certain objections to my criticism to which it is necessary for me to reply to prevent misinterpretation of my remarks, which were possibly too brief to be quite free from ambiguity. I refer to the third paragraph of the "Note." He begins by saying that he cannot agree with me that the expansion which he used is inadmissible. With respect to

* Communicated by the Author.

this, I have only to point out that I have nowhere said that it was inadmissible. I am not therefore concerned with his further statement regarding the expression of non-periodic functions by series of periodic functions: Fourier's representation of such functions in definite integral form is well known.

He goes on to say further, "I cannot agree with Mr. McCowan . . . . . that the form which he proposes at p. 58 to substitute, that of a series involving exponentials in which the coefficient of x in the index is real, is (at least for my purpose) admissible." It is "inadmissible, on account of the discontinuity of the expression." To this, again, I must reply that I have nowhere proposed to use any such series. To clear away whatever obscurity may remain, let me quote the part of the paper "On the Theory of Oscillatory Waves," which I have criticised in § 12 of my paper. In § 2 he says "the general integral of (2) $[\frac{d^2\phi}{dx^2}+\frac{d^2\phi}{dy^2}=0$, where ϕ is the velocity potential,] is

$$\phi=\Sigma \mathrm{A}\epsilon^{mx+ny},$$

the sign Σ extending to all values of A, m, and n, real or imaginary, for which $m^2+n^2=0$ . . . . . In the present case, the expression for ϕ must not contain real exponentials in x, *since a term containing such an exponential would become infinite either for* $x=-\infty$, *or for* $x=+\infty$, as well as its differential coefficients which would appear in the expressions for u and v [the components of the velocity]; so that m must be wholly imaginary."

The italics and the added explanations within square brackets are mine. I understand this to mean that it is only for the reason given that real exponentials are omitted. Remembering then the difference in the notation, that my "imaginary m" is his real m, and that my z is his y, and that my $\phi+\mathrm{U}x$ is practically his ϕ, refer to § 12 of my paper. I explain that he has "put aside imaginary values of the m as inadmissible," having "concluded that such a value would imply infinite velocity, &c., either when $x=+\infty$, or when $x=-\infty$;" and then I go on to criticise this view, saying "but this is not necessarily so . . . . . for in fact the value of ϕ given in (5)

$$\left[\phi+\mathrm{U}x=\mathrm{U}a\frac{\sinh mx}{\cos mz+\cosh mx}\right],$$

gives a well-known expansion

$$[\phi+\mathrm{U}x=\mathrm{U}a+2\mathrm{U}a\sum_{i=1}^{i=\infty}(-)^i\epsilon^{-mix}\cos miz$$

when x is positive, and

$$= \mathrm{U}a + 2\mathrm{U}a\Sigma(-)^i \epsilon^{mix} \cos miz$$

when x is negative,] of the form

$$\Sigma \mathrm{A} \epsilon^{px+qz},$$

such as is considered by Stokes; but the real coefficients p are *discontinuous, changing sign with* x, so that ϵ^{px} vanishes both for $x = +\infty$, and for $x = -\infty$."

I have here corrected a slight misprint in the exponential, which would, however, cause no difficulty. I have also added for the sake of clearness within square brackets the expansion to which reference only was made, and it may be noted that though I explain that (5) may be so expanded, I make no suggestion that such an expansion should or could conveniently be used.

LXV. *On Instability of Periodic Motion, being a continuation of Article on Periodic Motion of a Finite Conservative System*.* *By* Sir WILLIAM THOMSON†.

23. LET $\psi, \phi, \chi, \vartheta$, be generalized coordinates of a system; and let $\mathrm{A}(\psi, \phi, \ldots \psi', \phi', \ldots)$ be the action in a path (§ 2 above) from the configuration $(\psi', \phi', \ldots)$ to the configuration $(\psi, \phi, \ldots)$ with kinetic energy $(\mathrm{E}-\mathrm{V})$ with any given constant value for E, the total energy; V being the potential energy (§ 3 above), of which the value is given for every possible configuration of the system. Let $\nu, \xi, \eta, \zeta \ldots$ and $\nu', \xi', \eta', \zeta' \ldots$ be the generalized component momentums of the system as it passes through the configurations $(\psi, \phi, \ldots)$ and $(\psi', \phi', \ldots)$ respectively. If by any means we have fully solved the problem of the motion of the system under the given forcive* (of which V is the potential energy), we know A for every given set of values of $\psi, \phi, \ldots \psi', \phi', \ldots$; that is to say, it is a known function of $(\psi, \phi \ldots, \psi', \phi', \ldots)$. Then, by Hamilton's principle [Thomson and Tait's 'Natural Philosophy,' § 330 (18)], we have

$$\left.\begin{aligned} \nu &= \frac{d\mathrm{A}}{d\psi}, \quad \xi = \frac{d\mathrm{A}}{d\phi}, \quad \eta = \frac{d\mathrm{A}}{d\chi}, \quad \zeta = \frac{d\mathrm{A}}{d\vartheta}, \ldots \\ \nu' &= -\frac{d\mathrm{A}}{d\psi'}, \quad \xi' = -\frac{d\mathrm{A}}{d\phi'}, \quad \eta' = -\frac{d\mathrm{A}}{d\chi'}, \quad \zeta' = \frac{d\mathrm{A}}{d\vartheta'}, \ldots \end{aligned}\right\} \quad . \quad (1)$$

* Phil. Mag. Oct. 1891.

† Communicated by the Author, having been communicated to the Royal Society on the 26th of November, 1891.

‡ This is a term introduced by my brother, Prof. James Thomson, to denote a force-system.

24. Now let P′ P designate a particular path* from position $(\psi', \phi', \chi', \ldots)$ which for brevity we shall call P′, to position $(\psi, \phi, \chi, \ldots)$ which we shall call P. Let ${}_0\mathrm{P}'\ {}_0\mathrm{P}$ be a part of a known periodic path, from which P′ P is infinitely little distant. But first, whether ${}_0\mathrm{P}'\ {}_0\mathrm{P}$ is periodic or not, provided it is infinitely near to P′ P, and provided ${}_0\mathrm{P}'$ and ${}_0\mathrm{P}$ are infinitely near to P′, and P, respectively, we have, by Taylor's theorem, and by (1),

$$\left.\begin{aligned}
&\mathrm{A}(\psi, \phi, \chi, \ldots, \psi', \phi', \chi', \ldots) \\
&= \mathrm{A}({}_0\psi, {}_0\phi, {}_0\chi, \ldots, {}_0\psi', {}_0\phi', {}_0\chi', \ldots) \\
&\quad + {}_0\nu(\psi - {}_0\psi) + {}_0\xi(\phi - {}_0\phi) + \ldots - {}_0\nu'(\psi' - {}_0\psi') - {}_0\xi'(\phi' - {}_0\phi') - \ldots \\
&+ \tfrac{1}{2}\left\{ {}_0\left(\frac{d^2\mathrm{A}}{d\psi^2}\right)(\psi - {}_0\psi)^2 + {}_0\left(\frac{d^2\mathrm{A}}{d\phi^2}\right)(\phi - {}_0\phi)^2 + \ldots \right. \\
&\quad \left. + 2\,{}_0\left(\frac{d^2\mathrm{A}}{d\psi\, d\phi}\right)(\psi - {}_0\psi)(\phi - {}_0\phi) + \ldots \right\}
\end{aligned}\right\} \quad (2)$$

25. Let us now simplify by choosing our coordinates so that the values of ϕ, χ, &c., are each zero for every position of the path ${}_0\mathrm{P}'\ {}_0\mathrm{P}$; and let ψ, for any position of this path, be the action along it reckoned from zero at ${}_0\mathrm{P}'$. These assumptions, expressed in symbols, are as follows:—

$$\left.\begin{aligned}
&\frac{d\mathrm{A}}{d\phi} = 0, \quad \frac{d\mathrm{A}}{d\chi} = 0, \ldots \quad \frac{d\mathrm{A}}{d\psi} = -\dot{\psi}', \quad \frac{d\mathrm{A}}{d\phi'} = 0, \quad \frac{d\mathrm{A}}{d\chi'} = 0, \ldots \\
&\text{for all values of } \psi \text{ and } \psi', \text{ if } \phi = 0,\ \chi = 0, \ldots;\ \phi' = 0,\ \chi' = 0 \ldots
\end{aligned}\right\} \quad (3)$$

26. Taking now

$$\psi' = 0,\ \psi = {}_0\psi,\ {}_0\phi = 0,\ {}_0\chi = 0, \ldots\ {}_0\psi' = 0,\ {}_0\phi' = 0,\ {}_0\chi' = 0 \ldots\ldots\ldots \quad (4);$$

we have

$$\mathrm{A}({}_0\psi, {}_0\phi, {}_0\chi, \ldots, {}_0\psi', {}_0\phi', {}_0\chi', \ldots) = \mathrm{A}({}_0\psi, 0, 0, \ldots 0, 0, 0 \ldots) \quad (5)$$

* For any given value of E, the total energy (§ 3 above), the problem of finding a path from any position P′ to any position P is determinate. Its solution is, for each coordinate of the system, a determinate function of the coordinates which define P and P′ and of t, the time reckoned from the instant of passing through P′. The solution is single for the case of a particle moving under the influence of no force; every path being an infinite straight line. For a single particle moving under the influence of a uniform force in parallel lines (as gravity in small-scale terrestrial ballistics) the solution is duplex or imaginary. For every constrainedly finite system the solution is infinitely multiple: as is virtually well known by every billiard player for the case of a Boscovichian atom flying about within an enclosing surface, and by every tennis player for the parabolas with which he is concerned, and their reflexions from walls or pavement.

and, in virtue of this and of (3) and (1), (2) becomes

$$\begin{aligned} A({}_0\psi, \phi, \chi, \ldots, 0, \phi', \chi', \ldots) = A({}_0\psi, 0, 0, \ldots 0, 0, 0) \\ + \tfrac{1}{2}\big[{}_{11}\phi^2 + {}_{22}\chi^2 + {}_{33}\vartheta^2 + {}_{44}\phi'^2 + {}_{55}\chi'^2 + {}_{66}\vartheta'^2 \\ + 2({}_{12}\phi\chi + {}_{13}\phi\vartheta + {}_{14}\phi\phi' + {}_{15}\phi\chi' + {}_{16}\phi\vartheta' \\ {}_{23}\chi\vartheta + {}_{24}\chi\phi' + {}_{25}\chi\chi' + {}_{26}\chi\vartheta' \\ + {}_{34}\vartheta\phi' + {}_{35}\vartheta\chi' + {}_{36}\vartheta\vartheta' \\ + {}_{45}\phi'\chi' + {}_{46}\phi'\vartheta' \\ + {}_{56}\chi'\vartheta')\big] \end{aligned} \quad \Big\} \ldots (6)$$

where, merely for simplicity of notation, we suppose the total number of freedoms of the system, that is to say the total number of the coordinates ψ, ϕ, χ, ϑ, to be four; and for brevity put

$${}_0\left(\frac{d^2A}{d\phi^2}\right) = 11, \quad {}_0\left(\frac{d^2A}{d\phi d\chi}\right) = 12, \quad {}_0\left(\frac{d^2A}{d\chi^2}\right) = 22, \text{ \&c. } . \quad (7).$$

27. From (6) we find, by (1),

$$\left.\begin{aligned} \xi &= {}_{11}\phi + {}_{12}\chi + {}_{13}\vartheta + {}_{14}\phi' + {}_{15}\chi' + {}_{16}\vartheta' \\ \eta &= {}_{21}\phi + {}_{22}\chi + {}_{23}\vartheta + {}_{24}\phi' + {}_{25}\chi' + {}_{26}\vartheta' \\ \zeta &= {}_{31}\phi + {}_{32}\chi + {}_{33}\vartheta + {}_{34}\phi' + {}_{35}\chi' + {}_{36}\vartheta' \\ -\xi' &= {}_{41}\phi + {}_{42}\chi + {}_{43}\vartheta + {}_{44}\phi' + {}_{45}\chi' + {}_{46}\vartheta' \\ -\eta' &= {}_{51}\phi + {}_{52}\chi + {}_{53}\vartheta + {}_{54}\phi' + {}_{55}\chi' + {}_{56}\vartheta' \\ -\zeta' &= {}_{61}\phi + {}_{62}\chi + {}_{63}\vartheta + {}_{64}\phi' + {}_{65}\chi' + {}_{66}\vartheta' \end{aligned}\right\} \quad . \quad . \quad (8)$$

These equations allow us to determine the three displacements, ϕ, χ, ϑ, and the three corresponding momentums, ξ, η, ζ, for any position on the path, in terms of the initial values ϕ', χ', ϑ', ξ', η', ζ', supposed known.

28. To introduce now our supposition (§ 24) that ${}_0P'{}_0P$ is part of a periodic path; let Q be a position on it between ${}_0P'$ and ${}_0P$; and let us now, to avoid ambiguity, call it ${}_0P'\,Q\,{}_0P$. Let ${}_0P'$ and ${}_0P$ now be taken to coincide in a position which we shall call O; in other words, let ${}_0P'\,Q\,{}_0P$, or OQO, be the complete periodic circuit, or orbit as we have called it (§ 2 above). Our path P′P is now a path infinitely near to this orbit, and P′ and P are two consecutive positions in it for which ψ has the value zero. These two positions are infinitely near to one another and to O. We shall call them O_i, and O_{i+1}, considering them as the positions on our path in which ψ is zero for the ith time and for the $(i+1)$th time, from an earlier initial epoch than first passage through $\psi = 0$ which we

have been hitherto considering. It is accordingly convenient now to modify our notation as follows :—

$$\left.\begin{array}{l} \phi'=\phi_i, \quad \chi'=\chi_i, \quad \vartheta'=\vartheta_i\,; \quad \xi'=\xi_i, \quad \eta'=\eta_i, \quad \zeta'=\zeta_i \\ \phi=\phi_{i+1}, \chi=\chi_{i+1}, \vartheta=\vartheta_{i+1}\,; \quad \xi=\xi_{i+1}, \eta=\eta_{i+1}, \zeta=\zeta_{i+1} \end{array}\right\} \quad (9).$$

Here ϕ_i, χ_i, ϑ_i are the generalized components of distance from O, at the ith transit through $\psi=0$, of the system pursuing its path infinitely near to the orbit; and ξ_i, η_i, ζ_i are the corresponding momentum-components. With the notation of (9), equations (8) become equations by which the values of these components for the $i+1$th time of transit through $\psi=0$ can be found from their values for the ith time. They are equations of finite differences, and are to be treated *secundum artem*, as follows :—

29. Assume

$$\left.\begin{array}{lll} \phi_{i+1}=\rho\phi_i, & \chi_{i+1}=\rho\chi_i, & \vartheta_{i+1}=\rho\vartheta_i\,; \\ \xi_{i+1}=\rho\xi_i, & \eta_{i+1}=\rho\eta_i, & \zeta_{i+1}=\rho\zeta_i \end{array}\right\} \quad . \quad . \quad . \quad . \quad (10)$$

Substituting accordingly in (8) modified by (9), and eliminating ξ_i, η_i, ζ_i, we find

$$\left.\begin{array}{l} \left(11+\dfrac{14}{\rho}+41\rho+44\right)\phi+\left(12+\dfrac{15}{\rho}+42\rho+45\right)\chi+\left(13+\dfrac{16}{\rho}+43\rho+46\right)\vartheta=0 \\ \left(21+\dfrac{24}{\rho}+51\rho+54\right)\phi+\left(22+\dfrac{25}{\rho}+52\rho+55\right)\chi+\left(23+\dfrac{26}{\rho}+53\rho+56\right)\vartheta=0 \\ \left(31+\dfrac{34}{\rho}+61\rho+64\right)\phi+\left(32+\dfrac{35}{\rho}+62\rho+65\right)\chi+\left(33+\dfrac{36}{\rho}+63\rho+66\right)\vartheta=0 \end{array}\right\}.$$

Remarking that $41=14$, $12=21$, &c., we see that the determinant for the elimination of the ratios $\phi|\chi|\vartheta$ is symmetrical with reference to ρ and $1|\rho$. Hence it is

$$C_3(\rho^3+\rho^{-3})+C_2(\rho^2+\rho^{-2})+C_1(\rho+\rho^{-1})+2C_0, \quad . \quad (12)$$

where C_0, C_1, C_2, C_3 are coefficients of which the values in terms of 11, 12, &c. are easily written out. This determinant equated to zero gives an equation of the 6th degree for determining ρ, of which for each root there is another equal to its reciprocal. We reduce it to an equation of the third degree by putting

$$\rho+\rho^{-1}=2e. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Let e_1, e_2, e_3 be the roots of the equation thus found. The corresponding values of ρ are

$$e_1\pm\sqrt{(e_1^2-1)}\,;\ e_2\pm\sqrt{(e_2^2-1)}\,;\ e_3\pm\sqrt{(e_3^2-1)}. \quad . \quad (14)$$

In the case of e having any real value between 1 and -1, it is convenient to put

$$\left.\begin{aligned} e &= \cos\alpha, \\ \text{which gives} \quad \rho &= \cos\alpha + \iota\sin\alpha \\ \text{and} \quad \rho^{-1} &= \cos\alpha - \iota\sin\alpha \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

30. Suppose now, for the first time of passing through $\psi=0$, the three coordinates and three corresponding momenta, ϕ_1, χ_1, ϑ_1, ξ_1, η_1, ζ_1, to be all given; we find

$$\left.\begin{aligned} \phi_{i+1} &= A_1\rho_1{}^i + A_1'\rho_1{}^{-i} + A_2\rho_2{}^i + A_2'\rho_2{}^{-i} + A_3\rho_3{}^i + A_3'\rho_3{}^{-i} \\ \chi_{i+1} &= B_1\rho_1{}^i + B_1'\rho_1{}^{-i} + B_2\rho_2{}^i + B_2'\rho_2{}^{-i} + B_3\rho_3{}^i + B_3'\rho_3{}^{-i} \\ &\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\ &\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\ \zeta_{i+1} &= F_1\rho_1{}^i + F_1'\rho_1{}^{-i} + F_2\rho_2{}^i + F_2'\rho_2{}^{-i} + F_3\rho_3{}^i + F_3'\rho_3{}^{-i} \end{aligned}\right\}, \quad (16)$$

where A_1, A_1', A_2, A_2' . . . F_1, F_1', F_2, F_2' are 36 coefficients which are determined by the six equations (16), with $i=0$: and the six equations (8), modified by (9); with i successively put $=1, 2, 3, 4, 5$; with the given values substituted for ϕ_1, χ_1, ϑ_1, ξ_1, η_1, ζ_1, in them; and with for ϕ_2, χ_2, &c. their values by (16).

31. Our result proves that every path infinitely near to the orbit is unstable unless every root of the equation for e has a real value between 1 and -1. It does not prove that the motion *is* stable when this condition is fulfilled. Stability or instability for this case cannot be tested without going to higher orders of approximation in the consideration of paths very nearly coincident with an orbit.

[To be continued.]

Postscript, *November* 10, 1891.

The subject of periodic motion and its stability has been treated with great power by M. Poincaré in a paper, "Sur le problème des trois corps et les équations de la dynamique," for which the prize of His Majesty the King of Sweden was awarded on the 21st of January, 1889. This paper, which has been published in Mittag-Leffler's Acta Mathematica, 13, 1 and 2 (270 4to pp.), Stockholm 1890, only became known to me twelve days ago through Prof. Cayley. I am greatly interested to find in it much that bears upon the subject of my communication of last June to the Royal Society "On some test cases for the Maxwell-Boltzmann doctrine regarding Distribution of Energy;" particularly in p. 239, the following paragraph:—"On peut démontrer que dans le voisinage

d'une trajectoire fermée représentant une solution périodique, soit stable, soit instable, il passe une infinité d'autres trajectoires fermées. Cela ne suffit pas, en toute rigueur, pour conclure que toute région de l'espace, si petite qu'elle soit, est traversée par une infinité des trajectoires fermées, mais cela suffit pour donner à cette hypothèse un haut caractère de vraisemblance."* This statement is exceedingly interesting in connexion with Maxwell's fundamental supposition quoted in § 10 of my paper, "that the system if left to itself in its actual state of motion, will, sooner or later, pass through every phase which is consistent with the equation of energy;"† an assumption which Maxwell gives not as a conclusion, but as a proposition which "we may with considerable confidence assert, . . . except for particular forms of the surface of the fixed obstacle." It will be seen that Poincaré's "hypothesis, having a high character of probability," does not go so far as Maxwell's, which asserts that every portion of space is traversed *in all directions* by *every trajectory*. The conclusion which I gave in § 13, as seeming to me quite certain "that every mode differs infinitely little from being a fundamental mode," is clearly a necessary consequence of Maxwell's fundamental supposition; the truth of which still seems to me highly probable *provided exceptional cases are properly dealt with.*

I also find the following statement, pp. 100–101 :—"Il y aura donc en général n quantités α^2 distinctes. Nous les appellerons les *coefficients de stabilité* de la solution périodique considerée.

"Si ces n coefficients sont tous réels et négatifs, la solution périodique sera stable, car les quantités ξ_i et η_i, resteront inférieures à une limite donnée.

"Il ne faut pas toutefois entendre ce mot de stabilité au sens absolu. En effet, nous avons négligé les carrés des ξ et des η et rien ne prouve qu'en tenant compte de ces carrés, le résultat ne serait pas changé. Mais nous pouvons dire au moins que les ξ et η, s'ils sont originairement très petits, resteront très petits pendant très longtemps. Nous pouvons exprimer ce fait en disant que la solution périodique jouit, sinon de la stabilité *séculaire*, du moins de la stabilité *temporaire*." Here the conclusion of § 31 of my present paper is perfectly anticipated and is expressed in a most interesting manner. M. Poincaré's investigation and mine are as different as two investigations of the same subject could well be, and it is very satisfactory to find perfect agreement in conclusions.

* The "trajectoire fermée" of M. Poincaré is what I called a "fundamental mode of rigorously periodic motion," or "an orbit."

† "Scientific Papers," vol. ii. p. 714.

LXVI. *Notices respecting New Books.*

A Course of Experiments in Physical Measurement.—Part IV. *Appendix for the Use of Teachers. By* HAROLD WHITING, *Ph.D.* Boston, U.S.A. D. C. Heath and Co. 1891.

WITH the present volume Dr. Whiting's treatise on Practical Physics is brought to a conclusion. He discusses in it those portions of the subject which are primarily of more importance to the teacher than to the student, such as the cost of providing apparatus for the course described in the three previous volumes, and also the most suitable arrangement of tables in the laboratory in order that the teaching may be imparted with the maximum of convenience both to teacher and student. The author recommends that the practical work be preceded by a special lecture on the theory and practice of the experiment to be performed, these demonstrations being quite distinct from the ordinary formal course of lectures on Physics. It is an open question, and one which the author does not discuss, whether the experimental demonstrations ought to precede or follow the formal course; in the case of the more mathematical portions of Physics it seems to us advisable to interest the student by means of an experiment, before introducing him to the complete theory of it as given in the lecture course. This is especially the case with Mechanics. in which subject the formal lectures ought to follow the demonstrations and experiments rather than precede them.

A great portion of the volume is devoted to tables of actual observations and results obtained in each of the experiments previously described. Then follow lists of the experiments, a knowledge of which is required in the case of candidates for admission to Harvard University; this section is of course of greater interest to American teachers. The remainder of the volume is taken up by proofs of the mathematical formulæ used in the earlier part of the work.

In reviewing the treatise as a whole we think the author has done well to insist upon the necessity of always making measurements, whatever their nature may be, as exactly as possible, and of eliminating errors by taking the mean of several observations; so that with comparatively rough apparatus really valuable results may be obtained by a careful student. On the other hand, the work has one drawback which it shares in common with all text-books on practical Physics, namely, that the experiments described are supposed to be performed with apparatus of a special pattern, which other laboratories do not possess. To a large extent, therefore, the course of experiments in each laboratory is arranged in accordance with the form of the apparatus possessed by it, and such text-books as the present one only serve as general guides which must be supplemented by printed or manuscript notes. JAMES L. HOWARD.

LXVII. *Intelligence and Miscellaneous Articles.*

MOLECULAR THEORY OF DIFFUSION AND ELECTROLYSIS. BY E. RIECKE.

FOR a dilute solution of a body which is not an electrolyte, the concentration of which is constant in all plane layers which are at right angles to an axis (z-Axis), but is variable in the direction of this axis, the author finds that the excess of the molecules moving downwards (that is, the strength of the diffusion-current) is

$$S = \frac{lu}{3}\frac{\partial N}{\partial z};$$

in which l is the mean path of the dissolved molecules, u the molecular velocity, N the number of gramme-molecules in unit volume of the solvent; then S is the number of gramme-molecules which move through unit section in a second in the direction of decreasing concentration. The coefficient of diffusion k for the time of a day is therefore

$$k = 86400 \cdot lu/3.$$

Thus the author calculates:—

	k.	Molecular weight.	l in cm. 10^{-8}.
Urea	0·81	60	0·086
Chloral hydrate ...	0·55	165	0·094
Mannite	0·38	182	0·068
Cane-sugar	0·31	342	0·077

For electrolysis Prof. Riecke finds for the number Q_p of positive ions which pass in a second through unit section,

$$Q_p = \frac{N}{\tau_p}\frac{\epsilon l_p^{\,2}}{\mu_p u_p^{\,2}} Z;$$

in which N is the number of molecules in unit volume, ϵ the quantity of positive electricity united to each molecule, l the mean path, u the molecular velocity, μ the molecular weight, τ the time between two successive impacts of a molecule of the ion against a molecule of the solvent, and Z the E.M.F. in electrostatic measure. The suffix p signifies that the numbers refer to the positive ion; n in like

manner represents the negative ion. From this may be calculated the transfer-number and the conductivity. If, further, A is that quantity of hydrogen which is liberated in a second by a current of unit strength in electromagnetic measure, the molecular conductivity, L, expressed in electrochemical equivalents, is

$$L = \frac{1}{A}\left(\frac{l_p}{\mu_p u_p} + \frac{l_n}{\mu_n u_n}\right).$$

If U and V are the absolute mobilities of the ions, then $L = U + V$, and therefore

$$U = \frac{l_p}{A\mu_p u_p}, \quad V = \frac{l_n}{A\mu_n u_n}.$$

With the aid of the values of U and V given by Prof. Kohlrausch the author thus calculates:—

Positive Ions.

	H.	Li.	NH_4.	Na.	K.	Ag.
U 10^{13}	300	22·6	51	33·5	52	43
μ_p	1	7	18	23	39	107·7
l_p 10^3	0·82	0·16	0·59	0·44	0·89	1·22

Negative Ions.

	F.	CN.	Cl.	$C_2H_3O_2$.	NO_3.	Br.	ClO_3.	I.
V 10^{13}.....	32·4	54	53	24·8	49·6	57·2	43	57·2
μ_n	19	26	35·4	59	62	79·8	83·4	126·5
l_n 10	0·12	0·75	0·86	0·52	1·07	1·39	1·07	1·76

For the coefficient of diffusion of an electrolyte, finally, that is the number of gramme-molecules which with unit difference of concentration pass through unit section, the author finds

$$k = 40{\cdot}1(1 + 0{\cdot}00367t)n\mathrm{U} \times 10^{10},$$

in which n is the transfer-number, and U the absolute mobility of the ion in question. Thus for hydrochloric acid, $n = 0{\cdot}19$ and $\mathrm{U} = 300 \times 10^{-13}$, and therefore $k = 2{\cdot}44$. Observation gives 2·30. This example also proves the agreement between Riecke's equation and that which Nernst first gave for the connexion between the

conductivity and diffusion of an electrolyte.—*Zeitschrift für physikalische Chemie*, vol. vi. p. 564; *Beiblätter der Physik*, vol. xv. p. 370.

METHOD OF DETERMINING THE SURFACE-TENSION OF MERCURY.
BY H. SENTIS.

A rectangular plate of iron of the volume abc and the weight p floats on mercury; the actual dimensions were about $120 \times 8 \times 2$ c. millim. The depth h to which it sinks is determined by means of a spherometer. On the one hand, we have from the principle of Archimedes,

$$p = abh\mathrm{D} + 2(a+b)\mathrm{F}\cos\alpha;$$

in which D is the density of mercury, F the surface-tension, and α the edge-angle, and the second term on the right is the weight of the mercury which would fill up the groove about the plate. The error which is due to the corners may be eliminated by means of another plate of volume cde, and weight p', immersed to the same extent, which gives exactly the same error. On the other hand, the well-known equation

$$h = \sqrt{\frac{2\mathrm{F}}{\mathrm{D}}(1-\cos\alpha)}$$

holds, and by eliminating the error and the edge-angle we get the formula

$$\mathrm{F} = \frac{\mathrm{D}h^2}{4} + \frac{[p_1 - p_2 - (ab-cd)h\mathrm{D}]^2}{[d+b-c-d]^2 h^2 \mathrm{D}},$$

from which observations give F = 39·23 mg.—*Journal de Physique*, vol. ix. p. 384 (1890).

ALLOTROPIC SILVER.

Mr. M. Carey Lea requests us to correct a typographical error occurring in his paper, entitled "Notes on Allotropic Silver," which appeared in our October number. In this paper in several places appears "protochloride" where photochloride is the correct reading. Silver photochloride is the name proposed some years ago by Mr. Lea for the coloured compounds resulting from the union of normal silver chloride with small quantities of subchloride in no definite proportion, but after the manner of lakes as specially described by him.—The violet substance resulting from the exposure of silver chloride to light is a photochloride.

INDEX TO VOL. XXXII.

ACID, on a remarkable new, 400.
Allotropic silver, on, 337, 564.
Alloys, on changes of voltaic energy of, during fusion, 27.
Ames (J. S.) on homologous spectra, 319.
Ayrton (Prof. W. E.) on alternate current and potential difference analogies in the methods of measuring power, 204.
Azoimide, on, 400.
Bartoli (A.) on the measurement of the chemical intensity of the solar radiation, 480.
Basalt, on the specific heat of, 353.
Bell (A,) on some Post-Tertiary marine deposits, 140.
Bell, on the determination of the beats in the vibrations of a revolving, 370.
Blakesley's method of measuring power in transformers, on, 185.
Blondlot (R.) on the determination of the dielectric constant of glass, 230.
Bonney (Prof. T. G.) on the crystalline rocks of the Lizard district, 136.
Books, new:—Denning's Telescopic Work for Starlight Evenings, 127; Routh's Treatise on Analytical Statics, 129; Dixon's Foundations of Geometry, 130; Hermite's Explication de l'époch Quaternaire sans Hypothèses, 131; Becker's Structure of a portion of the Sierra Nevada of California, Antiquities from under Tuolumne Mountain in California, Notes on the Early Cretaceous of California and Oregon, 226, 227; Hagen's The Photochronograph and its application to Star-Transits, 228; Oliver, Wait, and Jones's Treatise on Trigonometry, Treatise on Algebra, 316; Jones's Logarithmic Tables, 316; Fine's Number-System of Algebra, 317; Hobson's Treatise on Plane Trigonometry, 317; Whiting's Course of Experiments in Physical Measurement, 396, 561; Backhouse's Structure of the Sidereal Universe, 397; Molenbroek's Theorie der Quaternionen, 477.
Boulder-clay, on wells in West-Suffolk, 228.
Callendar (H. L.) on the construction of platinum thermometers, 104.
Capacity, on a probable relationship between specific inductive, and latent heat of vaporization, 113.
Chalk, on a phosphatic, at Taplow, 134.
Charpentier (M.) on retinal oscillations, 397.
Chattock (A. P.) on the electrification of steel needle-points in air, 285.
Chemical action at a distance, on, 145, 478.
Chlorine, on the expansion of, by light as applied to the measurement of the intensity of rays of high refrangibility, 277.
Chree (C.) on some applications of physics and mathematics to geology, 233, 342.
Chronograph stylus, on a new form of, 383.
—— traces, on an instrument for measuring, 126.
Colour of pigments, on the influence of temperature on the, 401.
Colours, lecture-illustration of complementary, 399.
Compressibility of liquids, on an apparatus for measuring the, 79.
Cooper (W. J.) on the nature of solution, 473.
Crova, on the analysis of the light diffused by the sky, 141.
Curtius (T.) on a remarkable new acid, 400.
Davison (C.) on the Inverness earthquakes of 1890, 229.
Diamagnetic polarity, on the absurdity of, 192, 253, 318.

Dielectric constant of glass, on the determination of the, 230.
Diffusion, on the molecular theory of, 562.
Dissociation, on the theory of, 4, 20, 43, 75.
Dynamical problems in illustration of the theory of gases, 424.
Earthquakes of 1890, on the Inverness, 229.
Electrical oscillations on iron wires, on the damping of, 504.
Electricity, on the discharge of, in exhausted tubes without electrodes, 321, 445; on the velocity of, 480.
Electrification of steel needle-points in air, on the, 285.
Electrolysis, on some points in, 1; on the molecular theory of, 562.
Electrolytes, on the relation of volta electromotive force to latent heat, specific gravity, &c. of, 157.
Experiments, on the reduction of results of, 90, 99.
Fitzgerald (Prof. G.) on diamagnetism, 318.
Flamborough Head, on the drifts of, 133.
Flexure of beams, on the influence of surface-loading on the, 481.
Gases, on dynamical problems in illustration of the theory of, 424.
Gauss's theorem of curvatura integra, on a problem in plane kinetic trigonometry suggested by, 471.
Geological Society, proceedings of the, 133, 228.
Geology, on some applications of physics and mathematics to, 233, 342.
Glacial deposits at Hendon, on the, 139.
Glass, on the determination of the dielectric constant of, 230.
Glazebrook (R. T.) on the value of some mercury resistance standards, 70.
Gore (Dr. G.) on changes of voltaic energy of alloys during fusion, 27; on the relation of volta electromotive force to latent heat, specific gravity, &c. of electrolytes, 157.
Hatton (J. L. S.) on the determination of the beats in the vibrations of a revolving bell, 370.
Hayes (E. H.) on some of the objections raised to Mr. Pickering's methods of reducing experimental results, 99.
Hertz's experiment, on the influence of the size of the reflector in, 80.
Hicks (Dr. H.) on the glacial deposits at Hendon, 139.
Hill (Rev. E.) on wells in West-Suffolk boulder-clay, 228.
Hobson (B.) on the igneous rocks of the south of the Isle of Man, 135.
Holland (C. E.) on zonal spherical harmonics, 512.
Ignis fatuus, on the, 464.
Indicator for high speeds, on a steam-engine, 63.
Inferior oolite of the Cotteswolds, on a microscopic study of the, 138.
Iron, on some of the effects of magnetism on rods of, 383.
Iron wires, on the damping of electrical oscillations on, 504.
Irving (Rev. A.) on some recent excavations in the Wellington College district, 140.
Jennings (A. V.) on Manod and the Moelwyns, 133.
Johnstone (W.) on the nature of solution, 473.
Jones (P. R.) on zonal spherical harmonics, 512.
Kinetic theory of solids, on a, 31, 215, 524.
Klobukow (N. V.), lecture-illustration of complementary colours, 399.
Kohlrausch's theory of ionic velocity, on, 43.
Lamb (C. G.) on zonal spherical harmonics, 512.
Lamplugh (G. W.) on the drifts of Flamborough Head, 133.
Lea (M. C.) on allotropic silver, 337, 564.
Lehfeldt (R. A.) on a modified form of Wheatstone's bridge, 60.
Light diffused by the sky, on the analysis of the, 141.
——, on the expansion of chlorine by, as applied to the measurement of the intensity of rays of high refrangibility, 277.
Liquids, on an apparatus for measuring the compressibility of, 79.
Lister (J. J.) on the geology of the Tonga Islands, 229.
McCowan (J.) on the solitary wave, 45, 553.

McMahon (Major-General C. A.) on the crystalline rocks of the Lizard district, 136.
Magnetism, on the theory of, 192, 253, 318; on some of the effects of, on rods of iron, nickel, and other metals, 383.
Magneto-optic phenomenon, on Kerr's, 320.
Marr (J. E.) on the Cross Fell inlier, 135.
Melaphyres of Caradoc, on the, 229.
Mercury, on a method of determining the surface-tension of, 564.
Moelwyns, on the geology of the, 133.
Motion of a finite conservative system, on periodic, 375, 555.
Nichols (E. L.) on the influence of temperature on the colour of pigments, 401.
Nicholson (Prof. H. A.) on the Cross Fell inlier, 135.
Nickel, on some of the effects of magnetism on rods of, 383.
Obach (Dr. E.) on a relationship between specific inductive capacity and latent heat of vaporization, 113.
Obsidian, on a spherulitic and perlitic, 137.
Ostwald (Prof. W.) on chemical action at a distance, 145.
Parker (J.) on the theory of magnetism and the absurdity of diamagnetic polarity, 192, 253.
Periodic motion of a finite conservative system, on, 375, 555.
Perry (Prof. J.) on a steam-engine indicator for high speeds, 63; on the study of transformers, 168; on Mr. Blakesley's method of measuring power in transformers, 185; on a table of zonal spherical harmonics, 512.
Pfaundler (Prof.) on a method of determining specific heat by means of the electrical current, 232.
Phosphorus, on a new modification of, 365.
Pickering (S. U.) on the theory of dissociation into ions, 20; on Mr. Lupton's method of reducing the results of experiments, 90; on chemical action at a distance, 478.
Pigments, on the influence of temperature on the colour of, 401.
Platinum thermometers, on the construction of, 104.
Post-Tertiary marine deposits on the South Coast, on some, 140.
Power, on alternate current and potential difference analogies in the methods of measuring, 204.
Preston (S. T.) on an acoustic thermometer, 58.
Rayleigh (Lord) on dynamical problems in illustration of the theory of gases, 424.
Resistance standards, on the value of some mercury, 70.
Retinal oscillations, on, 397.
Richardson (Dr. A.) on the expansion of chlorine by light as applied to the measurement of the intensity of rays of high refrangibility, 277.
Riecke (E.) on the molecular theory of diffusion and electrolysis, 562.
Roberts-Austen (W. C.) on the specific heat of basalt, 353
Rocks, on the igneous, of the south of the Isle of Man, 135; on the crystalline, of the Lizard district, 136.
Rücker (Prof. A. W.) on the relation between the density and composition of dilute sulphuric acid, 304; on the specific heat of basalt, 353.
Rutley (F.) on a spherulitic and perlitic obsidian, 137; on the melaphyres of Caradoc, 229.
Salts, on the mutual solubility of, in water, 75.
Schuster (A.), electrical notes by, 9.
Sentis (H.) on a method of determining the surface-tension of mercury, 564.
Silver, on allotropic, 337, 564.
Sissingh (R.) on Kerr's magneto-optic phenomenon, 320.
Skinner (S.) on an apparatus for measuring the compressibility of liquids, 79.
Sky, on the analysis of the light diffused by the, 141.
Smith (F. J.) on an instrument for measuring chronograph traces, 126; on some of the effects of magnetism on rods of iron, nickel, and other metals which have received a permanent torsional set; and a new form of chronograph stylus, 383.

Snow (B. W.) on the influence of temperature on the colour of pigments, 401.
Solar radiation, on the measurement of the chemical intensity of the, 480.
Solids, on a kinetic theory of, 31, 215, 524.
Solution, on the theory of, 20, 90, 99, 304, 355, 473.
Specific heat, on a method of determining, by means of the electrical current, 232.
Spectra, on homologous, 319.
Steam-engine indicator for high speeds, on a, 63.
Steel needle-points, on the electrification of, in air, 285.
Stefan (Prof. J.) on Wheatstone's determination of the velocity of electricity, 480.
Stokes (Sir G. G.) on the theory of the solitary wave, 314; on the influence of surface-loading on the flexure of beams, 500.
Strahan (A.) on a phosphatic chalk at Taplow, 134.
Sulphuric acid, on the relation between the density and composition of dilute, 304.
Sumpner (Dr. W. E.) on alternate current and potential difference analogies in the methods of measuring power, 204.
Surface-loading, on the influence of, on the flexure of beams, 481.
Surface-tension of mercury, on a method of determining the, 564.
Sutherland (W.) on a kinetic theory of solids, 31, 215, 524.
Swinburne (J.) on some points in electrolysis, 1.
Temperature, on the influence of, on the colour of pigments, 401.
Thermometer, on an acoustic, 58.
Thermometers, on the construction of platinum, 104.
Thomson (Prof. J. J.) on the discharge of electricity in exhausted tubes without electrodes, 321, 445.
Thomson (Sir W.) on periodic motion of a finite conservative system; 375, 555; on a theorem in plane kinetic trigonometry, 471.
Tomlinson (C.) on the ignis fatuus, 464.
Tonga Islands, on the geology of the, 229.
Transformers, on the study of, 168; on Mr. Blakesley's method of measuring power in, 185.
Trevor (J. E.) on the mutual solubility of salts in water, 75.
Trigonometry, on a theorem in plane kinetic, 471.
Trouton (F. T.) on the influence of the size of reflector in Hertz's experiment, 80.
Trowbridge (J.) on the damping of electrical oscillations on iron wires, 504.
Vaporization, on a probable relationship between specific inductive capacity and latent heat of, 113.
Vector potential, on the, 9.
Velocity, on Kohlrausch's theory of ionic, 43.
Vernon (H. M.) on a new modification of phosphorus, 365.
Vibrations of a revolving bell, on the determination of the beats in a, 370.
Voltaic energy of alloys, on changes of, during fusion, 27.
Walker (Dr. J.) on the new theories of solution, 355.
Walker (J.) on the determination of the beats in the vibrations of a revolving bell, 370.
Wanklyn (Prof. J. A.) on the nature of solution, 473.
Wave, on the solitary, 45, 314, 553.
Wethered (E.) on a microscopic study of the Inferior Oolite of the Cotteswolds, 138.
Wheatstone's bridge, on a modified form of, 60.
Whetham (W. C. D.) on Kohlrausch's theory of ionic velocity, 43.
Wilson (E.) on a Rhætic section at Pylle Hill, 138.
Wilson (Prof. C. A. C.) on the influence of surface-loading on the flexure of beams, 481.
Young's modulus, on, 215.
Zonal spherical harmonics, table of, 512.

END OF THE THIRTY-SECOND VOLUME.

Printed by Taylor and Francis, Red Lion Court, Fleet Street.

BINDING ... MAR 19 1971

QC
1
P4
ser.5
v.32

The Philosophical magazine

Physical &
Applied Sci.
Serials

PLEASE DO NOT REMOVE
CARDS OR SLIPS FROM THIS POCKET

UNIVERSITY OF TORONTO LIBRARY